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**ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY**

***VOLUME 6***





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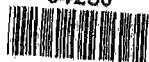
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**VOLUME 6**

**EXPLOSIVES to  
FURFURAL**

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## ABBREVIATIONS AND SYMBOLS

A.	Ångström unit(s)	b. (as, $b_H$ )	boiling (at 11 mm.)
abs.	absolute	B	base; as, $B.2HCl$
a.c.	alternating current	bbl.	barrel(s)
A.C.S.	American Chemical Society	Bé.	Baumé
addn.	addition	b.p.	boiling point
A.G.A.	American Gas Association	B.t.u.	British thermal unit(s)
A.I.Ch.E.	American Institute of Chemical Engineers	bu.	bushel(s)
alc.	alcohol, alcoholic	C.	centigrade
alk.	alkaline (not alkali)	C-	denoting attachment to carbon; as, <i>C</i> -alkyl derivatives of aniline
Alk	alkyl	cal.	calorie(s)
amp.	ampere(s)	calcd.	calculated
amp.-hr.	ampere-hour(s)	c.f.m.	cubic foot per minute
amt.	amount (noun)	cg.	centigram(s)
anhyd.	anhydrous	c.g.s.	centimeter-gram-second (system)
A.P.I.	American Petroleum Institute	chem.	chemical
app.	apparatus	<i>C.I.</i>	<i>Colour Index</i> No.
approx.	approximate (adj.), approximately	cm.	centimeter(s)
aq.	aqueous	coeff.	coefficient
Ar	aryl	com.	commercial
<i>ar-</i>	aromatic; as, <i>ar</i> -derivatives of tetralin	compd.	compound (noun)
<i>as-</i>	asymmetric; as, <i>as-m</i> -xylidine	compn.	composition
ASA	American Standards Association	concd.	concentrated
A.S.M.	American Society for Metals	concn.	concentration
A.S.M.E.	American Society of Mechanical Engineers	cond.	conductivity
A.S.T.M.	American Society for Testing Materials	const.	constant
atm.	atmosphere(s), atmospheric	cor.	corrected
at. wt.	atomic weight	c.p.	chemically pure
av.	average	crit.	critical
		cryst.	crystalline
		crystd.	crystallized
		crystn.	crystallization
		cu.	cubic
		d. (as, $d_4^{20}$ )	density (conveniently, specific gravity)
		<i>d</i>	differential operator
		<i>d-</i>	<i>dextro-</i> , dextrorotatory



D-	denoting configurational relationship, as to <i>de</i> - <i>tro</i> -glyceraldehyde	g.	gram(s)
		gal.	gallon(s)
d.b.	dry bulb	hp.	horsepower
d.c.	direct current	hr.	hour(s)
dec., decomp.	decompose(s)	hyd.	hydrated, hydrous
decompd.	decomposed	i.	insoluble
decompn.	decomposition	<i>i</i> -	inactive; as, <i>i</i> -methionine
deriv.	derivative		
detc.	determined	I.C.C.	Interstate Commerce Commission
detc.	determination		
diam.	diameter	I.D.	inner diameter
dielec.	dielectric (adj.)	in.	inch(es)
dil.	dilute	insol.	insoluble
distd.	distilled	I.U.	International Unit(s)
distn.	distillation	I.U.C.,	International Union of
DL-, <i>dl</i> -	racemic	I.U.P.A.C.	Chemistry, International Union of Pure and Applied Chemistry
dm.	decimeter		
<i>e</i>	electron		
ed.	edition, editor	j.	joule
elec.	electric, electrical	K.	Kelvin
elev.	elevated	<i>K</i>	dissociation constant
e.m.f.	electromotive force	kg.	kilogram(s)
eng.	engineering	kg.-cal.	kilogram-calorie(s)
eq.	equation	kv.	kilovolt(s)
equil.	equilibrium	kv.-amp.	kilovolt-ampere(s)
equiv.	equivalent	kw.	kilowatt(s)
esp.	especially	kw.-hr.	kilowatt-hour(s)
estd.	estimated	l.	liter(s)
estn.	estimation	<i>L</i> -	<i>levo</i> -, levorotatory
e.s.u.	electrostatic unit(s)	<i>L</i> -	denoting configurational relationship, as to <i>levo</i> -glyceraldehyde
e.u.	entropy unit(s)		
e.v.	electron volt(s)	lb.	pound(s)
expt.	experiment	LC <sub>50</sub>	concentration lethal to 50% of animals tested
exptl.	experimental		
ext.	extract	LD <sub>50</sub>	dose lethal to 50% of animals tested
extd.	extracted		
extn.	extraction	ln	logarithm (natural)
F.	Fahrenheit	log	logarithm (common)
Fedl.	Federal	m.	meter(s)
ff.	following (pages)	<i>m</i> -	meta; as, <i>m</i> -xylene
fig.	figure	M	metal
fl.oz.	fluid ounce(s)	<i>M</i>	molar (as applied to concn.; not molal, which is written out)
f.o.b.	free on board		
f.p.	freezing point		
ft.	foot (feet)		
ft.-lb.	foot-pound(s)		

ma.	milliampere(s)	ppt.	precipitate
manuf.	manufacture	pptd.	precipitated
manufd.	manufactured	pptn.	precipitation
manufg.	manufacturing	prepd.	prepared
max.	maximum	prepn.	preparation
m.c.f.	million cubic feet	p.s.i.(g.), (a.)	pound(s) per square inch (gage), (absolute)
m.e.	milliequivalent(s)	pt.	point
mech.	mechanical	pts.	parts
m.e.v.	million electron volts		
mg.	milligram(s)		
m.g.d.	million gallons per day	quad. pt.	quadruple point
min.	minimum; minute(s)	qual.	qualitative
misc.	miscellaneous	quant.	quantitative
mixt.	mixture	<i>q.v.</i>	"which see"
ml.	milliliter(s)	R	univalent hydrocarbon radical (or hydrogen)
M.L.D.	minimum lethal dose		
mm.	millimeter(s)	R.	Rankine
mol.	molecule, molecular	recrystd.	recrystallized
m.p.	melting point	recrystn.	recrystallization
m.p.h.	miles per hour	ref.	reference
M.R.	molar refraction	resp.	respectively
mv.	millivolt(s)	r.h.	relative humidity
mμ	millimicron(s)	<i>R.I.</i>	<i>Ring Index</i> No.
$n$ ( $n_D^{20}$ )	index of refraction (for 20°C. and sodium light)	r.p.m.	revolutions per minute
<i>n</i> -	normal; as, <i>n</i> -butyl	r.p.s.	revolutions per second
<i>N</i>	normal (as applied to concn.)	s.	soluble
<i>N</i> -	denoting attachment to nitrogen; as, <i>N</i> -meth- ylaniline	s-	symmetric(al) as, <i>s-m</i> - xyldine
		<i>S</i> -	denoting attachment to sulfur; as, <i>S</i> -methyl- cysteine
neg.	negative (adj.)	S.A.E.	Society of Automotive Engineers
no.	number		
N.O.I.B.N.	not otherwise indexed by name	satd.	saturated
		satn.	saturation
<i>o</i> -	ortho; as, <i>o</i> -xylene	S.C.F.	standard cubic foot (feet)
<i>O</i> -	denoting attachment to oxygen; as, <i>O</i> -acetyl- hydroxylamine	sec.	second(s)
		<i>sec</i> -	secondary; as, <i>sec</i> -butyl
O.D.	outer diameter	S.F.s.	Saybolt Furol second(s)
oz.	ounce(s)	sl.s.	slightly soluble
		sol.	soluble
p., pp.	page, pages	soln.	solution
<i>p</i> -	para; as, <i>p</i> -xylene	soly.	solubility
pos.	positive (adj.)	sp.	specific
powd.	powdered	spec.	specification
p.p.m.	parts per million	sp.gr.	specific gravity

spp.	species	X.U. ( $10^{-10}$	X-unit
sq.	square	mm.)	
S.T.P.	standard temperature		
	and pressure	yd.	yard(s)
subl.	sublime(s), subliming	yr.	year(s)
S.U.s.	Saybolt Universal		
	second(s)	°	degree
<i>sym</i> -	symmetric(al); as, <i>sym</i> -	%	per cent
	<i>m</i> -xylidine	$[\alpha]_D^{20}$	optical rotation (for
			20°C. and sodium
tech.	technical		light)
temp.	temperature		
<i>tert</i> -	tertiary; as, <i>tert</i> -butyl	$\gamma$	microgram(s)
theoret.	theoretical	$\partial$	differential operator
t.p.h.	tons per hour		(partial)
Twad.	Twaddell	$\Delta$	finite difference
		$\eta$	viscosity
v.	volt(s)	$\lambda$	wave length
<i>vic</i> -	vicinal; as, <i>vic-m</i> -xyli-	$\mu$	micron(s)
	dine	$\Omega$	ohm(s)
vol.	volume(s) (not volatile)	<	less than
v.s.	very soluble	>	more than
w.	watt(s)	$\sim$	cycle(s)
wt.	weight	$\approx$	approximately equal to

Other letter symbols may be found in "Standard System of Nomenclature for Chemical Engineering Unit Operations" adopted by the American Institute of Chemical Engineers.

## SHIPPING REGULATIONS

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- White label (for acids and corrosive liquids)
- Red label (for inflammable compressed gases)
- Green label (for noninflammable compressed gases)
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## PERIODICAL ABBREVIATIONS

The abbreviations used are, for the most part, those given in the "List of Periodicals Abstracted by Chemical Abstracts" (Vol. 40, No. 24, Pt. 2 (1946), also published separately). Some of the journals most frequently referred to are the following:

*Am. Soc. Testing Materials, Proc.*  
*Anal. Chem.* (superseding *Ind. Eng. Chem., Anal. Ed.*)  
*Angew. Chem.* (superseding *Z. angew. Chem.; Chemie, Die*)  
*Ann.*  
*Ann. Rev. Biochem.*  
*Ber.* (see also *Chem. Ber.*)  
*Biochem. J.*  
*Biochem. Z.*  
*BIOS Repts.*  
*Bull. soc. chim. or Bull. soc. chim. France*  
*Bur. Standards J. Research* (see also *J. Research Natl. Bur. Standards*)  
*C.A.*  
*Can. J. Research*  
*Chem. Ber.* (superseding *Ber.*)  
*Chem. Eng.* (superseding *Chem. & Met. Eng.*)  
*Chem. Eng. News* (superseding *News Ed. (Am. Chem. Soc.)*)  
*Chem. Eng. Progress* (superseding *Trans. Am. Inst. Chem. Engrs.*)  
*Chem. Fabrik* (see also *Chem. Tech. (Berlin), Ver. Chem. App.*)  
*Chemie, Die* (see also *Angew. Chem.*)  
*Chem. Inds.*  
*Chemistry & Industry*  
*Chem. & Met. Eng.* (see also *Chem. Eng.*)  
*Chem. Revs.*  
*Chem. Tech. (Berlin), Ver. Chem. App.* (superseding *Chem. Fabrik*)  
*Chem. Zentr.*  
*Chem.-Ztg.*

*Chimica e industria (Italy) or Chimica e industria (Milan)*  
*Chimie & industrie*  
*CIOS Repts.*

*Elec. Eng.*  
*FIAT Repts.*  
*Gazz. chim. ital.*  
*Helv. Chim. Acta*  
*Ind. Chemist*  
*Ind. Eng. Chem.; Anal. Ed.* (see also *Anal. Chem.*); *News Ed.* (see also *News Ed. (Am. Chem. Soc.); Chem. Eng. News*)

American Society for Testing Materials, Proceedings  
 Analytical Chemistry

Angewandte Chemie

Annalen der Chemie, Justus Liebig's  
 Annual Review of Biochemistry  
 Berichte der deutschen chemischen Gesellschaft  
 Biochemical Journal, The  
 Biochemische Zeitschrift  
 British Intelligence Objectives Subcommittee Reports  
 Bulletin de la société chimique de France  
 Bureau of Standards Journal of Research

Chemical Abstracts  
 Canadian Journal of Research  
 Chemische Berichte  
 Chemical Engineering with Chemical & Metallurgical Engineering  
 Chemical and Engineering News

Chemical Engineering Progress with Transactions of American Institute of Chemical Engineers  
 Chemische Fabrik, Die

Chemie, Die  
 Chemical Industries  
 Chemistry & Industry  
 Chemical & Metallurgical Engineering  
 Chemical Reviews  
 Chemische Technik, Die (Berlin), Vereinigt mit Chemische Apparatur  
 Chemisches Zentralblatt  
 Chemiker-Zeitung mit dem Sonderteil, Die Chemische Praxis, und der Beilage, Chemisch-technische Übersicht  
 Chimica, La, e l'industria (Italy) or (Milan)

Chimie & industrie  
 Combined Intelligence Objectives Subcommittee Reports  
 Electrical Engineering  
 Field Information Agency Technical Reports  
 Gazzetta chimica italiana  
 Helvetica Chimica Acta  
 Industrial Chemist and Chemical Manufacturer, The  
 Industrial and Engineering Chemistry; Analytical Edition; News Edition

- J. Am. Chem. Soc.*  
*J. Am. Med. Assoc.*  
*J. Am. Pharm. Assoc.*  
*J. Applied Chem. (U.S.S.R.)*  
*J. Assoc. Offic. Agr. Chemists*  
  
*J. Biol. Chem.*  
*J. Chem. Physics*  
*J. Chem. Soc.*  
*J. Colloid Sci.*  
*J. Electrochem. Soc.* (superseding *Trans. Electrochem. Soc.*)  
*J. Ind. Hyg. Toxicol.*  
*J. Inst. Metals*  
  
*J. makromol. Chem.* (superseding *J. prakt. Chem.*)  
*J. Org. Chem.*  
*J. Phys. Chem.* (see also *J. Phys. & Colloid Chem.*)  
*J. Phys. & Colloid Chem.* (superseding *J. Phys. Chem.*)  
*J. Polymer Sci.* (superseding *J. Polymer Research*)  
*J. prakt. Chem.* (see also *J. makromol. Chem.*)  
*J. Research Natl. Bur. Standards* (superseding *Bur. Standards J. Research*)  
*J. Sci. Food Agr.*  
*J. Soc. Chem. Ind. or J. Soc. Chem. Ind. (London)* (see also *Chemistry & Industry*)  
*Kolloid-Z.*  
*News Ed. (Am. Chem. Soc.)* (superseding *Ind. Eng. Chem., News Ed.*; see also *Chem. Eng. News*)  
*Office Tech. Services (OTS) Repts.* (superseding *Office Publication Board Repts.*)  
*Rec. trav. chim.*  
*Revs. Modern Phys.*  
*Trans. Am. Electrochem. Soc.* (see also *Trans. Electrochem. Soc.*; *J. Electrochem. Soc.*)  
*Trans. Am. Inst. Chem. Engrs.* (see also *Chem. Eng. Progress*)  
*Trans. Am. Inst. Mining Met. Engrs.*  
  
*Trans. Electrochem. Soc.* (superseding *Trans. Am. Electrochem. Soc.*; see also *J. Electrochem. Soc.*)  
*Z. angew. Chem.* (see also *Angew. Chem.*; *Chemie, Die*)  
*Z. anorg. Chem.* (see also *Z. anorg. u. allgem. Chem.*)  
*Z. anorg. u. allgem. Chem.* (see also *Z. anorg. Chem.*)  
*Z. Elektrochem.*  
  
*Z. physik. Chem.*
- Journal of the American Chemical Society, The  
 Journal of the American Medical Association, The  
 Journal of the American Pharmaceutical Association  
 Journal of Applied Chemistry (U.S.S.R.)  
 Journal of the Association of Official Agricultural Chemists  
 Journal of Biological Chemistry, The  
 Journal of Chemical Physics, The  
 Journal of the Chemical Society (London)  
 Journal of Colloid Science  
 Journal of the Electrochemical Society  
  
 Journal of Industrial Hygiene and Toxicology, The  
 Journal of the Institute of Metals and Metallurgical Abstracts  
 Journal für makromolekulare Chemie  
  
 Journal of Organic Chemistry, The  
 Journal of Physical Chemistry, The  
  
 Journal of Physical & Colloid Chemistry, The  
  
 Journal of Polymer Science  
  
 Journal für praktische Chemie  
  
 Journal of Research of the National Bureau of Standards  
 Journal of the Science of Food and Agriculture  
 Journal of the Society of Chemical Industry (London)  
  
 Kolloid-Zeitschrift  
 News Edition (American Chemical Society)  
  
 Office of Technical Services Reports  
  
 Recueil des travaux chimiques des Pays-Bas  
 Reviews of Modern Physics  
 Transactions of the American Electrochemical Society  
  
 Transactions of the American Institute of Chemical Engineers  
 Transactions of the American Institute of Mining and Metallurgical Engineers  
 Transactions of the Electrochemical Society, Inc.  
  
 Zeitschrift für angewandte Chemie  
  
 Zeitschrift für anorganische Chemie  
  
 Zeitschrift für anorganische und allgemeine Chemie  
  
 Zeitschrift für Elektrochemie und angewandte physikalische Chemie  
 Zeitschrift für physikalische Chemie

# *E* continued

## EXPLOSIVES

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An explosive may be defined as a substance that can undergo very rapid, exothermic, self-propagating decomposition with the formation of more stable products. The explosive substance may be caused to undergo explosion by heat, impact, friction, or the detonation wave from another explosive. An explosive may be solid, liquid, or gaseous, but generally is a solid. It may consist of a single chemical compound or a mixture of explosive compounds or of one or more explosive compounds with nonexplosive material.

The products of explosion generally consist of gases, or in some cases, gases and solids. Examples of such explosives are nitroglycerin and lead azide, respectively. In a few cases, such as copper acetylide, the products of explosion are nongaseous and any explosive value of the material depends upon its heating effect on adjacent gases. The gaseous products of explosion generally have a volume much greater than that of the explosive itself.

Invariably, an explosion results in the liberation of a considerable amount of heat, this being sufficient to propagate the explosion from the initial point or area throughout the mass. The heat liberated also raises the products of explosion to a very high temperature, thus developing high gas pressures, which can be applied to doing work. The work done by an explosive is determined primarily by the amount of heat given off during explosion.

An important characteristic of almost all explosives is oxygen balance, which is the oxygen content relative to the total oxygen required for oxidation of all carbon, hydrogen, and other easily oxidizable elements to carbon dioxide, water, etc. Oxygen balance is expressed either as percentage of total oxygen required or as percentage of oxygen in excess or deficient. A few explosives, such as lead azide, involve no oxidation reactions and cannot be said to have an oxygen balance. Some examples of the calculation of oxygen balance follow:



## 2 EXPLOSIVES

Explosive	Oxygen balance
$C_2H_4N_2O_6 \longrightarrow 2 CO_2 + 2 H_2O + N_2$ glycol dinitrate	100% or 0%
$C_3H_5N_3O_9 \longrightarrow 3 CO_2 + 2\frac{1}{2} H_2O + \frac{1}{2} O_2 + 1\frac{1}{2} N_2$ nitroglycerin	105.9% or +5.9%
$C_4H_8N_2O_7 + 5 O \longrightarrow 4 CO_2 + 4 H_2O + N_2$ diethylene glycol dinitrate	58.3% or -41.7%

The definition of an explosive given above is general for this type of material, but actually covers two distinct classes of materials. One of these undergoes autocombustion at rates that vary from a few inches per minute to approximately 400 meters per second. Examples of these are colloided nitrocellulose and black powder. Materials of this class can be used as *propellants* or for strictly explosive effects, and technically are termed *low explosives*. The second class comprises those materials that undergo detonation or decomposition, which is almost instantaneous. The rates of detonation of such explosives vary from 1000 to 8500 m./sec. Examples are dynamite and Cyclonite. Materials of this class are termed *high explosives* and generally are referred to when the term explosives is used in technical literature. It is of interest to note that certain materials, such as nitrocellulose, can be made to undergo the relatively slow autocombustion typical of propellants or the detonation typical of high explosives.

Propellants are subdivided chiefly on the basis of composition, but high explosives fall into two categories on the basis of their relative ease of initiation to detonation. One of these consists chiefly of compounds that are sufficiently sensitive to heat, impact, or friction to undergo detonation or combustion when subjected to such physical forces. These materials, because they possess more or less capacity to transmit a detonation wave to less sensitive explosives, are termed *initiating explosives*, *initiating agents*, or *initial detonating agents*. Examples of initiating agents are mercury fulminate and lead azide. The remaining high explosives, which are too insensitive to be detonated in practice by the brief application of heat or by impact or friction, comprise the greatest number of this category. They are used for both military and industrial purposes, and TNT and dynamites are examples of this category of high explosives.

Propellants are suitable for use in obtaining propulsive effects because the rate of burning can be so controlled that excessive pressures are avoided, and the pressures developed can be applied so as to obtain desired ballistic effects. If such control of burning rate is not obtained, the development of excessive pressure may lead to the transformation of combustion into detonation with consequent rupture of the gun or rocket and loss of ballistic effect.

High explosives other than initiating explosives were originally used for industrial blasting operations, their use for this purpose being preceded by that of the low explosive black powder. Today they are used industrially for blasting, demolition, and excavation purposes. In military operations, they are applied so as to obtain desired fragmentation, air-blast, underwater shock, penetration, and demolition effects. The formulation and application of high explosives have become highly developed techniques, which are still undergoing improvement, and the future attainment of a higher level of explosive potential is a possibility.

In the organization of this article, first consideration is given to black powder,

although this oldest of explosives is no longer used as a propellant and only to a limited extent as an explosive. Priming compositions, which are used to ignite propellants and initial detonating agents by means of a sudden burst of flame (not by a detonation wave) are considered next. The initiating and noninitiating high explosives that form the bulk of modern explosives are treated individually. Almost all blasting explosives can be classified as high explosives, but the fact that black powder is used for blasting necessitates the separate consideration of blasting explosives. Because of the factor of cost, blasting explosives usually differ markedly from military high explosives with respect to composition. Propellants form the last group considered because of the fact that, like blasting explosives, in general they contain chiefly compounds that are considered separately as high explosives.

Only the most important members of each class of explosives are covered. Finally, brief descriptions are given of the tests used for determining the explosive characteristics described. For descriptions of less important explosives and details of manufacture, analysis, testing, and application, the reader is referred to more exhaustive texts listed in the bibliography. See also *Explosions*.

### BLACK POWDER

Black powder is a mechanical mixture of potassium or sodium nitrate, charcoal, and sulfur. Standard black powder is made with potassium nitrate; black blasting powder (see p. 61), with sodium nitrate. Black powder has been known for at least 700 years and probably much longer. It was used first for pyrotechnic, incendiary, and demolition effects, and it was not until the invention of the gun that its value as a propellant was recognized. With the development of the gun, black powder became the universal explosive. When ignited by a torch or spark from a flint, a loose charge of black powder above the borehole or in the priming pan served as a priming composition. The charge of black powder in the borehole acted as a fuse composition to advance the ignition to the propellant charge of black powder in the tube of the gun. When the projectile was of the shrapnel type, black powder in the delay fuze was ignited and in turn ignited the bursting charge of black powder. Up to 1870 black powder was in general use for propellant and blasting purposes; however, its general replacement as a propellant was soon to come, and its displacement as a blasting explosive by nitroglycerin and dynamite had already begun. Today it is used chiefly in ignition charges for smokeless powder, saluting charges, delay charges in military time fuzes and blasting (miner's) fuse, and for blasting in open operations such as quarries.

Because of the large number of disastrous explosions that have occurred, the manufacture of black powder is carried out in a series of buildings carefully spaced so as to prevent the propagation of explosion or fire from one building to another. The general method of manufacture is as follows:

In one house the potassium nitrate is ground in a ball mill, while the charcoal and sulfur are pulverized together in a ball mill located in another house. The sulfur thereby is "incorporated" or worked into the cellular openings of the charcoal. The nitrate and charcoal-sulfur mixture are transferred to a mixing building, where they are sieved to remove foreign materials and then mixed. Mixing is accomplished by dampening the materials and mixing by hand or mechanically. The mixed materials are transferred to a millhouse containing a wheel mill. Each of the two wheels, made of cast iron, is 7-8 ft. in diameter, has a width of 18 in., and weighs approximately 10 tons. The wheels are so assembled that the path of one overlaps that of the other by several inches. A plough behind the inner wheel is turned so as to throw the material being mixed away from the center of the mill, while a plough behind the outer wheel throws the material toward the center. About 300 lb. of mix-

ture is spread on the bed of the wheel mill and moistened so as to contain approximately 4% of moisture. The mill then is operated for 4-6 hours at the rate of 10 r.p.m. This milling operation serves to increase the degree of incorporation of the nitrate and sulfur into the charcoal.

At the conclusion of the milling operation, any wheel cake or clinker is broken up manually. The milled material then is transferred to a presshouse and pressed into cakes 18-24 in. square and 0.75-1 in. thick. This is done by means of a hydraulic press with a spread of about 6 ft. between platens, and aluminum plates 0.37 in. thick. The powder is placed on the plates and an aluminum rack is used to hold the powder in place while the depth of layer is adjusted. Successive layers and plates are built up until about 400 lb. of powder has been put in the press. Pressure of 6000 p.s.i. then is applied for a period varying with the type of powder desired.

The resulting cakes are transferred to a corning mill building, being unloaded in a room that is partitioned off from the corning mill by a steel barricade. The cakes are fed into the mill by means of a conveyor, which carries them over the top of the barricade. The first rolls of the mill have corrugated surfaces and are adjustable. The broken cakes then are fed to another pair of rolls that further reduces the material to the desired grain size. The powder then passes over mechanically operated shaker screens, the dust and fines being caught in bags. This material is returned to the wheel mill. The coarse material from the screens is passed through the rolls a second time and rescreened. The corning mill operation is considered the most hazardous in the manufacture of black powder.

After being transferred to the blending house, the powder is placed in rotating drums of hardwood about 8 ft. long and 4 ft. in diameter. Tumbling of the powder results in heating because of friction, temperatures as high as 65°C. being developed. This heating causes evaporation of any moisture present and no further drying of the powder is necessary. If the powder is to be glazed, graphite is added to the contents of the drum after the moisture has been reduced to a certain point, but before the powder becomes too dry. The experience of the operator is depended upon for this. Drying and glazing require approximately 8 hours. The powder is separated into standard granulations by sieving before packing. The finished powder is packed in airtight kegs that hold 20-25 lb. of powder and usually are made from thin metal.

**TABLE I. Standard Military Black Powders.**

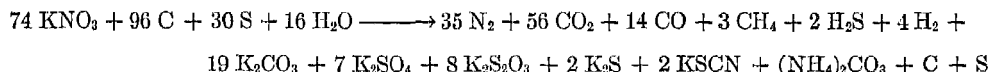
Constituent	Potassium nitrate type	Sodium nitrate type
Potassium nitrate, %.....	74.0	—
Sodium nitrate, %.....	—	71.0
Charcoal, %.....	15.6	16.5
Sulfur, %.....	10.4	12.5

Standard military black powders have the compositions given in Table I. Black powders burn at rates dependent upon composition, degree of incorporation, density, and degree of confinement. The sodium nitrate powder is slower burning than that containing potassium nitrate. Increase in the percentage of nitrate at the expense of the percentage of charcoal causes a decrease in the burning rate. A small change in the sulfur content does not affect the rate of burning, but moisture in excess of 0.2% causes decrease in this. The type of charcoal has a pronounced effect on the rate of burning, powders made from willow or alder charcoal burning much more rapidly than those made from oak charcoal. Powders made by simple mixing burn much more slowly than incorporated powder, the rate increasing with increase in incorporation. Increase in grain density has the effect of decreasing the rate of burning. At a pressure of 25,000 p.s.i., black powder burns at a rate of approximately 4 in./sec., as compared with rates of 7-12 in./sec. for single- and double-base smokeless powders. Efforts to cause detonation of black powder by initiation with a booster explosive have yielded a maximum rate of approximately 400 m./sec., as compared with rates from 4000 to 8500 m./sec. for high explosives. This may be considered as due to the explo-

sion of black powder representing an exothermic reaction between ingredients, rather than the exothermic decomposition of a compound as in the case of TNT.

For some applications it is desirable that black powder burn at a rate somewhat less than that normal for the standard composition at atmospheric pressures. This usually is accomplished by changing the type of charcoal used, substituting barium nitrate for potassium nitrate, increasing the proportion of sulfur present, or by inclusion of inert materials such as borax.

The burning of black powder is assumed to take place in accordance with the following approximate empirical equation:



Combustion takes place with the liberation of approximately 680 kg.-cal. of heat per kilogram and the formation of 600 grams of solids and 278 liters of gas.

In the absence of excessive moisture, black powder is of a high order of chemical and physical stability. The ingredients of the powder are essentially nonreactive with each other even at temperatures as high as 120°C. However, it is not desirable to heat black powder above 70°C. because of the rapid increase in vapor pressure of the sulfur, with consequent increase in volatility and change in composition or uniformity of composition of the powder.

Black powder is undesirably hygroscopic, the sodium nitrate type being even more so than the standard potassium nitrate type. The hygroscopicity has been found to vary widely with the conditions of exposure to atmospheric humidity. This hygroscopicity has been attributed generally to the presence of potassium or sodium nitrate, each of which is known to be hygroscopic. While the nitrate does contribute to the hygroscopicity of black powder, it has been found that the charcoal is chiefly responsible for this. Evidently the large specific surface of the charcoal, with its known adsorptive capacity for gases, is responsible for the high degree of hygroscopicity. The substitution of noncellular carbon, such as soot or sugar carbon, yields powder of much lower hygroscopicity. Such powders, because the sulfur and nitrate cannot be incorporated into the particles of carbon, are much less satisfactory with respect to uniformity of burning rate and burn much less rapidly than the powder made with charcoal. Powder used for military purposes is required to contain not more than 0.7% of moisture, and in practice powder generally is dried so as to contain 0.2–0.3% immediately before use.

Black powder has a relatively low rate of burning and low heat of explosion and gas volume values as compared with high explosives such as TNT, and is thus much inferior to high explosives from the viewpoints of brisance and explosive power. In the sand test for brisance it crushes no sand when ignited by a flame and only 8 grams when initiated with Tetryl or PETN, as compared with 48 grams crushed by TNT. Because of the poor confinement in the Trauzl lead block test, the value for black powder is only 10% that for TNT. The ballistic mortar test indicates black powder to be 50% as powerful as TNT.

The recognized hazards involved in the manufacture and handling of black powder might indicate the material to be dangerously sensitive to impact or friction as well as ignition. Tests show that standard black powder is less sensitive to impact than Tetryl. Pendulum friction tests of black powder, with a steel shoe, have shown it to be quite insensitive to friction, no ignition resulting. The explosion temperature test

value of  $457^{\circ}\text{C}.$  for black powder ( $\text{TNT} = 475^{\circ}\text{C}.$ ) would indicate it to be relatively insensitive to ignition. However resistant black powder may be to ignition by non-radiant thermal energy, it is very susceptible to ignition by a flame, incandescent particle, or electric spark. In the manufacture and handling of black powder it is customary to go to extremes in the grounding of machinery, wearing of nailless shoes, etc., to avoid the formation of sparks of any type.

**Ignition Powder.** The standard potassium nitrate composition given in Table I is used for ignition purposes in military ammunition. The powder is granulated so as to pass through a No. 4 and be retained on a No. 8 screen. It is loaded in a cloth bag attached to the base of a charge of smokeless powder or is loaded in a tubular metal primer, with wall perforations, which is embedded in the smokeless powder charge. In some cases the black powder is pressed to form pellets before it is loaded in the primers.

The presence of a large number of finely divided, incandescent, solid particles in the products of explosion of black powder makes it an efficient ignition agent for smokeless powder. It has been found that black powder is more effective for the ignition of smokeless powder than is burning smokeless powder itself. This superiority of black powder, in spite of the higher heat and gas volume values of smokeless powder, may be attributable in part to the fact that the maximum temperature developed by black powder is somewhat greater than that for smokeless powder.

**Fuse Powder.** This is powder used in commercial miners' fuse, which is used for delays in exploding detonators (blasting caps). The powder may have the standard potassium nitrate composition given in Table I or represent a variation in the proportion of ingredients so as to decrease the rate of burning. In some cases, inert diluents such as graphite, brick dust, or borax may be present and serve to decrease the rate of burning.

**Fuze Powders.** These are black or modified black powder compositions that are loaded in the time-train rings of military time fuzes and serve to cause a predetermined delay between firing of the round and detonation of the charge in the shell or bomb. In order to obtain maximum uniformity of burning at a minimum rate, the powder is loaded in the rings under high pressures. It has been found that the effect of loading pressure on the density of the standard powder is as follows:

Loading pressure, 1000 p.s.i. ....	3	5	10	20	30	50	75	100
Density .....	1.32	1.408	1.55	1.695	1.775	1.84	1.88	1.88

If a lesser rate of burning is required than is obtainable with the standard black powder composition, the desired rate may be obtained by modifying the composition or by blending the standard powder with a powder that burns too slowly for direct use in fuzes. Modification of the composition in this direction can be accomplished by substitution of barium nitrate for part of the potassium nitrate in the standard composition. Resort must then be had to blending the modified powder with the standard powder in experimentally determined proportions. A powder that has a very low burning rate and can be blended with standard black powder contains 70% potassium nitrate, 14% bituminous coal, and 16% sulfur. The manufacture of such a coal powder is similar to that of standard black powder, but, because of the noncellular structure of bituminous coal, there is no incorporation of the nitrate and sulfur.

**Sodium Nitrate Powders.** These powders are distinctly more hygroscopic than standard black powder. When used for industrial purposes, they are glazed well with

graphite, which retards the absorption of moisture and renders their use practical. For military uses sodium nitrate powder is loaded in airtight assemblies. In this manner it can be used in saluting charges and practice bombs. Sodium nitrate black powder burns more slowly than standard black powder and is cheaper, so it is more suitable for use in certain types of mining and quarrying operations (see "Blasting explosives," p. 60).

**Miscellaneous.** Standard black powder is used to some extent as base charges for fuzes, in friction primers, as smoke-puff charges, in practice projectiles, and in delay elements in fuzes. It is an important material in the fabrication of fireworks (see *Pyrotechnics*).

The development of explosives since 1860 has resulted in the replacement of black powder by superior substitutes for specific purposes, so that today the use of black powder is relatively limited. With recent developments such as the VT fuze and new types of nonhygroscopic low-order explosives, it may be expected that the use of black powder will decrease still further, and perhaps disappear altogether.

## PRIMING COMPOSITIONS

Priming compositions are required to provide a sudden burst of flame to ignite an initial detonating agent, a propellant, a fuze powder, or a pyrotechnic composition. Their action is thus distinct from that of initial detonating agents, which are used to set up a detonation wave in high explosives. Priming compositions must function when subjected to impact, stab action, percussion, friction, or flame, and are used in commercial and military devices such as blasting caps, fuzes, small-arms cartridges, artillery and rocket igniters, incendiary compositions, and pyrotechnic compositions.

A priming composition must deliver a relatively large volume of hot gas and solid particles without the development of a detonating wave. The ideal priming composition would consist of a single chemical compound of uniform granulation that would undergo rapid, highly exothermic decomposition when subjected to one of the physical forces mentioned. To date the only compound meeting this requirement is lead dinitroresorcinate, but the sensitivity of the material is such that it can be used in the desired manner only under somewhat restricted conditions.

The next most desirable type of priming composition would be a mixture of compounds that, while individually nonexplosive, sensitize each other to ignition and rapid burning. Such compositions have been developed and will be discussed. In practice, most priming compositions consist of mixtures of one or more initial detonating agents with oxidizing agents, fuels, sensitizers, and binding agents. Potassium chlorate, antimony sulfide, and gum arabic are examples of the classes of addends mentioned. In some cases an addend may serve two purposes; in the above example antimony sulfide acts as both a fuel and a sensitizer to friction, while gum arabic acts as both a fuel and binding agent. The net effect of the addends is to so dilute the initial detonating agent as to convert its decomposition from detonation into rapid combustion. The addends may also serve to increase the volume of gas produced per unit weight of priming composition, to prevent the gases from having too high a temperature, and to contribute incandescent solid particles to the products of decomposition.

Table II gives examples of typical priming compositions. Priming compositions that consist of mixtures of nonexplosive ingredients are given as group A compositions. Among the earlier priming compositions, which were based on mercury fulminate as

the sensitive and explosive ingredient, are those listed as group B compositions. Another type of composition (group C) consisted of a mixture of nonexplosive ingredients and a small amount of an explosive not of the initial detonating agent class or a larger amount of a weak explosive of the initial detonating class. The replacement of mercury fulminate with lead azide and DDNP in detonators has led to the corresponding substitution of lead azide in priming compositions (group D). Such compositions are much more stable than those containing mercury fulminate.

TABLE II. Typical Priming Compositions.

Constituent	1	2	3	4
A. Mixtures of nonexplosive ingredients				
Potassium chlorate, %.....	55	60	50.5	—
Lead thiocyanate, %.....	45	—	—	—
Antimony sulfide, %.....	—	30	26.3	—
Cuprous thiocyanate, %.....	—	3	—	—
Sulfur, %.....	—	7	8.8	—
Ground glass, %.....	—	—	12.4	—
Shellac, %.....	—	—	2.0	—
B. Mixtures based on mercury fulminate				
Mercury fulminate, %.....	19	32	28	11
Potassium chlorate, %.....	33	45	14	52.5
Antimony sulfide, %.....	43	23	21	36.5
Black powder, %.....	2.5	—	—	—
Sulfur, %.....	2.5	—	—	—
Ground glass, %.....	—	—	35	—
Shellac, %.....	—	—	2	—
C. Mixtures of nonexplosive ingredients with noninitiating or weak initiating explosives				
Potassium chlorate, %.....	53	52.7	—	—
Lead thiocyanate, %.....	25	24.8	—	—
Antimony sulfide, %.....	17	11.9	5	—
Barium nitrate, %.....	—	—	42	—
Calcium silicide, %.....	—	—	18	—
TNT, %.....	5	—	—	—
PETN, %.....	—	9.9	—	—
Lead styphnate, %.....	—	—	35	—
Gum, %.....	—	0.7	—	—
D. Mixtures based on lead azide				
Potassium chlorate, %.....	53	33.4	—	—
Lead thiocyanate, %.....	25	—	—	—
Antimony sulfide, %.....	17	33.3	—	—
Silicon carbide, %.....	—	5.0	—	—
Lead azide, %.....	5	28.3	—	—

The classes of compositions given in Table II are intended for use where ignition is caused by impact, stab action, or percussion. In addition, compositions in certain assemblies are required to function through friction. An example is the friction primer for a pyrotechnic flare. This consists of a braided wire coated with red phosphorus and shellac, which is pulled through a pellet consisting of 88% potassium chlorate, 10% charcoal, and 2% dextrin. Other friction primers consist of a roughened wire or rod,

which is pulled through a pellet of priming composition. A typical composition of this type consists of 56.2% potassium chlorate, 24.6% antimony sulfide, 9.0% sulfur, and 10.2% ground glass.

Of the compositions listed in Table II, those containing mercury fulminate are the least stable, but even those may be considered satisfactory in this respect if not stored at temperatures above those normally encountered in temperate climates. The other compositions, containing nonexplosive compounds only or lead styphnate, lead azide, TNT, or PETN, are of a high order of stability even at 100°C. The presence of moisture may cause some acceleration of deterioration and, in some cases, lead to segregation and nonuniformity. As priming compositions are used frequently in conjunction with a water-wet binding agent, subsequent thorough drying of the composition is important. Binding agents in use include gum tragacanth, gum arabic, glue, dextrin, and sodium alginate.

The sensitivity of priming compositions varies widely, but that of an individual composition can be varied somewhat by careful control of the granulation of each of the ingredients. This, in some cases, is more important than the proportions of the ingredients. Nonuniformity of composition due to mechanical segregation of ingredients can cause great variations in sensitivity and failures to function. The presence of a binding agent prevents such segregation and fixes the composition in the desired position in an assembly.

The weight of priming composition used may be of the order of only 0.15 gram, and the rate of burning, volume of gases and weight of solid particles produced, and the duration of the flame are the characteristics of major importance in connection with efficient functioning. The volume of gas, at S.T.P., is of the order of only 1.5 ml. The percentage of the weight of the composition carried as incandescent particles by the hot gases will vary with the composition, but is approximately 70% in the case of the above composition containing 5% of TNT. Such incandescent particles are considered to promote ignition by thermal radiation.

The bursts of flame from various primer compositions loaded similarly have been found to have effective durations varying from 400 to 750 microsec., with total durations varying from 650 to 1500 microsec. Short as these times may appear, they are thousands of times as great as that which would be required for detonation of a composition of equal thickness. The priming composition in a round of military ammunition must function with the great speeds indicated by the above duration values. This can be recognized from the fact that in a 75-mm. round only 0.05 sec. is required for ignition, burning of the black powder igniter charge, and complete controlled combustion of the propellant charge.

## HIGH EXPLOSIVES

### Initial Detonating Agents

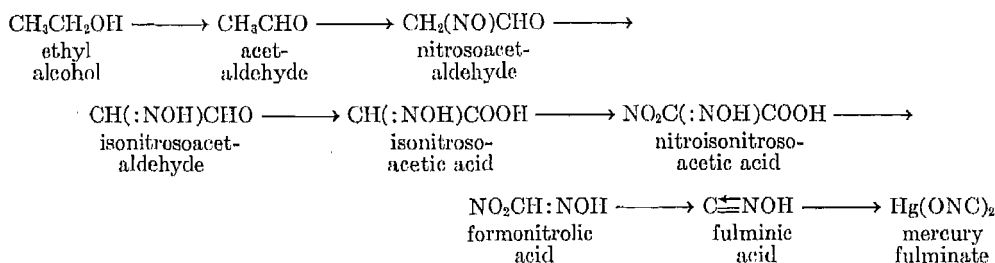
This class of compounds and mixtures is distinguished from high explosives such as dynamites and booster, bursting charge, and demolition explosives by the much greater ease with which they can be detonated by heat, impact, or friction. Most initial detonating agents have distinctly lower rates of detonation and brisance values than those of the explosives they are used to initiate; and, in most cases, initial detonating agents are of a lower order of stability. Certain compounds that might serve



as initial detonating agents are too sensitive or unstable to be of practical use, so that those actually in use during past or present times are within a relatively limited range of sensitivity and are few in number.

**Mercury fulminate**,  $\text{Hg}(\text{ONC})_2$ , formula weight 284.65, was first prepared by Johann Kunckel von Löwenstern (1630–1703), but Howard in 1800 first described its preparation and properties in detail. However, it was not until 1864, when Nobel used it to insure the explosion of nitroglycerin, that it was used as an initiator for the detonation of another explosive.

Although it can be prepared from acetaldehyde or nitromethane, mercury fulminate is generally prepared by the reaction of mercury, ethyl alcohol, and nitric acid. The intermediate products of the oxidation and nitration reactions involved appear to be:



In the manufacture of mercury fulminate the following procedure has been found to be satisfactory:

To 8–10 lb. of nitric acid (sp.gr. 1.4) in a 2-l. flask is added 1 lb. of redistilled mercury. The flask and contents, maintained at 55–60°C. by means of a bath of warm water, are allowed to stand overnight or until all the mercury has dissolved to form a solution of mercuric nitrate in excess acid. From the nitrating room this solution is transferred to the “fulminate room,” where it is poured into 8–10 lb. of 95% ethyl alcohol contained in a large (18–20 in. diameter) balloon flask. The flask, resting in a bath of running cold water, is immediately connected to a suction system, which removes any fumes evolved. The reaction begins immediately, with the evolution of white fumes. If colored nitrogen oxide fumes appear, the reaction is considered too violent and is checked by the addition of some ethyl alcohol. At the end of 1½ hours the reaction is considered complete, and when the contents of the flask have cooled to room temperature all of the fulminate has crystallized. The material in the flask is caught on a cloth screen and washed with cold running water until free from acid and until all fine impurities (“fulminate mud”) have been removed. The washed fulminate is transferred to cloth bags, which are stored in crocks or concrete tanks of water or packed in barrels of wet sawdust for shipment.

The yield of mercury fulminate is from 120 to 130 parts per 100 parts of mercury. The fumes from the reaction are drawn through condensers, and the condensed liquid is processed for the recovery of ethyl alcohol and aldehyde. Ethyl nitrate, ethyl nitrite, and nitroethane also are formed. The acid mother liquor from the reaction and water washings are neutralized with alkali, evaporated, and processed for any mercury present.

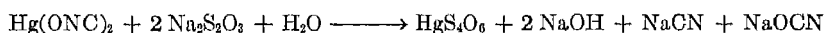
Pure mercury fulminate is white, but the material produced by the foregoing process is grayish and only 97–99% pure. It occurs as octahedral crystals. If a small amount of cupric chloride is added to the nitric acid solution of mercury, the color is improved, but there is no improvement in purity. Military specifications require a minimum purity of 98.0%. The impurities consist chiefly of metallic mercury and complex, water-insoluble compounds. Mercury fulminate can be purified by solution in aqueous potassium cyanide, pyridine, or aqueous ammonia and precipitation with

strong acid, water, or 70% nitric acid, respectively. The last method is considered preferable and yields a white product of 99.75% or greater purity.

Mercury fulminate has a crystal density of 4.42 but an apparent density of 1.35–1.75. When subjected to pressures of 3000, 10,000, 20,000, and 50,000 p.s.i., densities of 3.0, 3.6, 4.0, and 4.3 are obtained. Increasing pressure has the effect of desensitization so that, after being pressed at 25,000–30,000 p.s.i. or more, the "dead-pressed" fulminate merely ignites and burns when subjected to a flame. However, dead-pressed mercury fulminate is initiated to detonation at a high rate if it is covered with loose or slightly compressed fulminate or other initiating compound and this is ignited.

Mercury fulminate crystallizes from water with half a molecule of water of crystallization, but is anhydrous when crystallized from alcohol or precipitated from aqueous ammonia with nitric acid. Soluble to the extent of only 0.01% in water at 15.5°C. and only slightly soluble in alcohol, mercury fulminate is stored under water or, in cold weather, under a 50–50 mixture of water and ethyl alcohol or methanol. It is dried easily and is essentially nonhygroscopic (0.02% at 30°C. and 90% r.h.). Drying may be expedited by rinsing with ethyl alcohol or methanol.

The purity of mercury fulminate may be determined by dissolving in a measured excess of sodium thiosulfate and titrating with potassium iodide the thiosulfate remaining after completion of the reaction:



Starch solution is used as the indicator. A solution of sodium thiosulfate can be used for the disposal by decomposition of waste or deteriorated mercury fulminate, since only nonexplosive products are formed.

When a single crystal of mercury fulminate is ignited, it burns very rapidly with an intense flash, but does not undergo the high-order detonation that occurs when a layer of only a few crystals' thickness is ignited. When pressed at 3000 p.s.i., it has a rate of detonation of 3975 m./sec. and, when pressed at 30,000 p.s.i., its rate is 5400 m./sec. Mixtures of mercury fulminate with oxidizing agents such as potassium chlorate detonate at comparable rates; however, mixtures with inert materials and/or fuels merely burn rapidly, and such mixtures comprise a number of priming compositions.

Mercury fulminate is among the most sensitive of initial detonating agents to impact, friction, stab action, and heat. Table III gives comparative impact and explosion temperature test data. It can be used in a wide variety of manners in ammunition without involving extreme hazard in loading operations. While not as effective an initiator as lead azide or DDNP, its efficiency is such that excessive amounts are not required. The brisance (shattering effect) value of mercury fulminate is greater than that of lead azide, but less than that of DDNP, as shown by a comparison of the sand test values in Table III.

During the period 1865 to 1930 numerous efforts were made to develop a superior substitute for mercury fulminate because of the cost and semistrategic nature of mercury and the unsatisfactory stability of mercury fulminate. The standard grade (98–99% pure) of mercury fulminate deteriorates significantly even at 30–35°C., but it will remain of satisfactory purity and initiating value for some years if the storage temperature is not greater than 20°C. It has been found that the purity is reduced as follows at various storage temperatures:

Storage temperature, °C.	Time, in months, required to reduce purity to	
	95.0%	90.0%
80 .....	0.016	0.05
50 .....	8.25	12
30-35.....	20	40

Mercury fulminate purified so as to be 99.75% pure requires storage at 50°C. for 24 months to be reduced to 95.0% purity and for approximately 30 months to be reduced to 90.0% purity. When mercury fulminate has been reduced in purity to approximately 92%, its initiating efficiency is essentially lost, although it will still undergo explosion when ignited.

The successful development of lead azide and DDNP has resulted in their substitution for mercury fulminate in many applications; however, mercury fulminate is still used to some extent in commercial blasting caps and military ammunition.

**Fulminate-Chlorate Mixtures.** Mercury fulminate is relatively expensive, and the admixture of other materials was soon attempted, using oxidizing agents on account of the marked lack of oxygen balance of mercury fulminate. After the early use of black powder and potassium nitrate, potassium chlorate was introduced. It was found that 80-20 and 90-10 fulminate-chlorate mixtures are superior to fulminate alone with respect to initiating value, brisance, and safety in handling. By 1910 the use of these mixtures instead of fulminate in commercial detonators was general, and some use is still made of them. However, with the displacement of mercury fulminate by lead azide and DDNP, the use of fulminate-chlorate mixtures has declined correspondingly.

**Silver fulminate**,  $\text{Ag}_2(\text{ONC})_2$ , formula weight 299.80, has never attained commercial importance because of its greater cost and sensitivity than mercury fulminate. It has been used to a certain extent in the manufacture of fireworks and similar materials, such as snaps and pull-crackers.

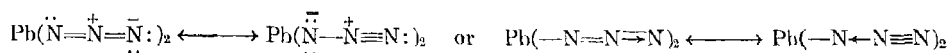
Silver fulminate is prepared by dissolving 1 part of silver in a mixture of 8.5 parts of nitric acid (sp. gr. 1.42) and 1.2 parts of water, with heating at 90-95°C., and adding the solution to 12.25 parts of 95% ethyl alcohol. The final mixture must have a temperature somewhat above 60°C. The silver fulminate precipitates as the reaction proceeds, the rate of reaction depending upon the temperature maintained. A practically quantitative yield of fulminate is obtained.

Unlike mercury fulminate, silver fulminate as ordinarily produced consists of fine amorphous aggregates instead of crystals. While normally it is slightly less sensitive to impact and more sensitive to heat than mercury fulminate, it has been found that under certain conditions of temperature some small clusters of crystals are formed that are much more sensitive than the amorphous aggregates. This explains the general conclusion that silver fulminate is dangerously sensitive.

Silver fulminate is a much more efficient initiator of detonation than mercury fulminate, and has essentially the same brisance as mercury fulminate as judged by the sand test.

**Lead azide**,  $\text{Pb}(\text{N}_3)_2$ , formula weight 291.26. Hydrazoic acid and its salts of lead, silver, and mercury were first prepared by Curtius in 1890 and 1891. As usually prepared, the lead salt consists of needlelike crystals, but it has been shown that lead azide exists in an orthorhombic ( $\alpha$ ) form having an absolute density of 4.71 and a monoclinic ( $\beta$ ) form having a density of 4.93. The  $\beta$ -form is much the more sensitive, and the two forms differ in rate of decomposition when heated. Lead azide can be produced also in the form of finely divided amorphous aggregates.

The structure of lead azide is essentially covalent. There is resonance between the two structures which may be shown in either of the two following ways:



Thus there is a smaller resonance energy and hence less stability than in the purely ionic forms found in the alkali azides (see *Hydrazoic acid*).

Efforts to produce crystalline lead azide for military and commercial uses began in 1893, but resulted in disastrous explosions. The manufacture of this material was continued only in France and Switzerland. Later it was adopted in England. Since World War I in Germany and since 1931 in the U.S., an amorphous form of lead azide has been produced that consists of rounded aggregates and contains a binding agent. This form, known as "dextrinated lead azide," has the following approximate composition: lead azide, 93%; lead hydroxide, 4%; dextrin and impurities, 3%.

The crystalline  $\alpha$ -form of lead azide is produced by the slow addition of a dilute solution of sodium azide to a dilute, constantly stirred solution of lead acetate or nitrate. Amorphous lead azide is prepared by the very rapid mixing of more concentrated solutions. Dextrinated lead azide is prepared by adding slowly a slightly alkaline solution of sodium azide to a solution of lead nitrate and dextrin. The precipitated lead azide is washed with water and stored in the same manner as mercury fulminate.

Pure lead azide consists of colorless crystals, while the dextrinated azide has a yellowish-white tint and has no crystal faces observable under a magnification of 50. The apparent densities of crystalline and dextrinated lead azide are approximately 0.8 and 1.8, respectively. The materials have density values of 2.9 and 2.6 when pressed at 3000 p.s.i. Density values as high as 4.05 can be obtained by higher loading pressures, but there is no evidence of desensitization (dead-pressing) by high pressures such as that characteristic of mercury fulminate.

Lead azide is soluble in water to the extent of only 0.02% at 18°C. and 0.05% at 100°C. It is essentially insoluble in ethyl alcohol, and can be stored under water or a mixture of water and ethyl alcohol. The hygroscopicity values for crystalline and dextrinated lead azide are 0.03% and 0.16%, respectively.

The purity of lead azide can be determined by treating a weighed quantity with ceric ammonium nitrate (ammonium nitratocerate) and measuring the nitrogen evolved. Waste lead azide can be decomposed so as to leave no explosive residue by treatment with a cold 10% solution of sodium hydroxide for 16 hours or treatment with a solution of ceric ammonium nitrate. Other methods involve solution in aqueous ammonium acetate and treatment with sodium dichromate, or suspension of the azide in sodium nitrite solution and the addition of nitric acid.

Individual crystals or aggregates of lead azide do not burn as do those of mercury fulminate, but they detonate as do larger quantities. If the crystals exceed 0.1 mm. in length, they may detonate when merely broken, so that control of crystal size is of the greatest importance. When pressed at 3000 p.s.i., lead azide detonates at a rate of 4300 m./sec., and at a density of 4.0 the rate is approximately 5100 m./sec.

As shown by Table III, lead azide is less sensitive to impact and heat than mercury fulminate. It also is less sensitive to friction, as shown by stab-action tests. As would be expected, dextrinated lead azide is less sensitive than the crystalline form. This lesser sensitivity of lead azide as compared with mercury fulminate has limited to some extent the applicability of lead azide, and has led to the superimposition in some cases of a more easily ignitable material such as lead styphnate.

Although lead azide has a slightly lower rate of detonation, is less brisant, and has

less explosive power, it is a markedly better initiator of detonation than mercury fulminate. It is also superior with respect to stability, as indicated by the results of tests at 100°C. given in Table III. Lead azide remains unimpaired after storage at 80°C. for 15 months, while at 80°C. the purity of mercury fulminate is reduced to 90% in 1.5 days.

Since lead azide is preferable to mercury fulminate with respect to stability, cost, and availability of raw materials, it has replaced mercury fulminate to a considerable extent in commercial blasting caps and military ammunition. Its disadvantages are that it is slightly less ignitable and sensitive to impact than is desirable under certain conditions. In addition, it is not quite as efficient an initiator of detonation as is DDNP.

**Silver azide**,  $\text{AgN}_3$ , formula weight 149.90, is obtained by a method very similar to that used for the preparation of crystalline lead azide, but the product consists of fine amorphous aggregates that vary widely in size. This material is of the same order of sensitivity to impact as crystalline lead azide but is much more sensitive to heat. When heated at 251°C. it melts and decomposes into silver and nitrogen, but when heated suddenly to only slightly higher temperatures it detonates. Silver azide is a slightly better initiator of detonation than lead azide, but the relatively high cost of the silver compound has prevented extensive use of the material.

**Diazodinitrophenol** (DDNP, 4,6-dinitrobenzene-2-diazo-1-oxide), considered by some to have a cyclic diazo oxide grouping (formula (I); see also Vol. 5, p. 41), formula weight 210.11, was first prepared by Griess, but it was not until Delm in 1922 patented its use as an explosive in mixtures that it was considered seriously for such use.

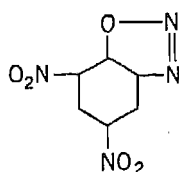
DDNP is a yellow or reddish-yellow amorphous powder, which is prepared by diazotizing picramic acid,  $\text{NH}_2(\text{NO}_2)_2\text{C}_6\text{H}_2\text{OH}$ , with sodium nitrite and hydrochloric acid. The dark brown, granular product is washed thoroughly with ice water and may be purified by dissolving it in hot acetone and precipitating by means of a large volume of ice water. With an absolute density of 1.63, DDNP in the loose form has an apparent density of 0.5–0.9. When pressed at 3000 p.s.i., it has a density of approximately 1.2, and it can be subjected to loading pressures as great as 130,000 p.s.i. without being desensitized.

DDNP is soluble in water to the extent of only 0.08% at 25°C., but it is soluble in methanol and ethyl alcohol at 50°C. to the extent of 1.25 and 2.43 grams per 100 grams of solvent. It is nonhygroscopic and may be stored under water or mixtures of water and alcohol. DDNP is soluble in acetone, nitroglycerin, nitrobenzene, aniline, pyridine, and acetic acid. DDNP may be decomposed, with the evolution of nitrogen, by treatment with a 0.5% solution of sodium hydroxide; this method is suitable for the disposal of waste or surplus material.

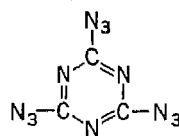
Contact with a flame results in the mere flashing of unconfined DDNP, but when the DDNP is confined, ignition results in detonation. It has a rate of detonation of 6900 m./sec. at a density of 1.58 (essentially that of TNT at the same density) and a calculated rate of 7100 m./sec. at density of 1.63. As shown by Table III, DDNP is as sensitive to impact as mercury fulminate, but is more sensitive to heat than either mercury fulminate or lead azide. This makes for ease of ignition and so renders it slightly more adaptable for use than lead azide. As judged by the sand test (Table III), DDNP has brisance essentially equal to that of TNT and twice that of mercury fulminate. No other known initiating agent has a greater brisance than DDNP. It has far greater explosive power than either mercury fulminate or lead azide as measured

by the Trauzl lead block test. The stability of DDNP is considerably better than that of mercury fulminate. Storage tests have shown that DDNP withstands storage at 50°C. for at least 30 months, as compared with 9 months for mercury fulminate, and storage under water at 50°C. for 12 months. DDNP is not as stable as lead azide, but is considered to be satisfactory for practical use. The initiating value of DDNP is considerably greater than that of either lead azide or mercury fulminate, as indicated by determined minimum detonating charges for pressed charges of Tetryl. This superiority is indicated also by the ability of DDNP to detonate ammonium picrate or cast TNT, neither of which can be detonated with lead azide or mercury fulminate.

Like lead azide, DDNP today has replaced mercury fulminate to a large extent in commercial blasting caps and to some extent in ammunition. By the use of either of these superior substitutes, the objections of high cost, critical supply of raw material, "dead-pressing," and poor stability previously involved in the use of mercury fulminate have been overcome.



(I)



(II)

**Tetracene** (4-guanyl-1-(nitrosoaminoguanyl)-1-tetrazene (*C.A.*)),  $\text{ON.NH.NH.C}(:\text{NH}).\text{N}:\text{N.NH.NH.C}(:\text{NH}).\text{NH}_2$ , formula weight 188.16, is a compound having peculiar explosive properties, which was first prepared by Hoffmann and Roth. It is prepared by the treatment of 1-aminoguanidine hydrogen carbonate or sulfate with sodium nitrite. Two molecules of the amino compound and two of nitrous acid react with coupling and the substitution of a nitrous group for an amino hydrogen. In practice, 27.6 grams of sodium nitrite is added to a solution, at 30°C., of 34 grams of 1-aminoguanidine hydrogen carbonate and 15.7 grams of glacial acetic acid in 2500 ml. of water. After 24 hours the precipitated Tetracene is caught on a filter and washed thoroughly with water. It is dried at room temperature.

Tetracene is a pale yellow, fluffy, crystalline solid that has an apparent density of only 0.5 and a density of only 1.05 when pressed at 3000 p.s.i. It is practically insoluble in water or most of the common organic solvents. It is hygroscopic to the extent of only 0.8%, but is decomposed by boiling water with the evolution of 2 molecules of nitrogen per molecule of Tetracene. It is decomposed by aqueous sodium hydroxide. It can be stored under water or a mixture of water and an alcohol.

When exposed to contact with a flame, Tetracene undergoes mild explosion with the production of much black smoke. It has an ignition temperature considerably lower than that of mercury fulminate, although the two compounds are of the same order of sensitivity to impact (Table III). It is in the ease of its ignition, high heat of explosion (663.5 cal./gram), and large volume of gaseous products of explosion that Tetracene is of practical importance in the application of explosives, since it has relatively little direct initiating value. It cannot be used to initiate TNT or Tetryl, although it can detonate loose or pressed PETN.

Tetracene is extremely subject to "dead-pressing." In the sand test the loose

material crushes 13.1 grams of sand. When loaded under increasing pressures, the brisance value decreases to 2 grams with a loading pressure of 3000 p.s.i., but Tetracene pressed at 3000 p.s.i. crushes 21.1 grams of sand when initiated with mercury fulminate. The brisance of the compound therefore depends upon its physical condition and mode of initiation.

The stability of Tetracene is not as great as would be desirable. It decomposes rapidly at 100°C. but appears to be relatively stable at temperatures not greater than 75°C. Tetracene has found use in priming compositions and cover charges for initiating agents less easy to ignite. A mixture of lead azide and Tetracene has been found satisfactory for charges in explosive rivets.

**Cyanuric triazide (II)**, formula weight 204.13, is an initiating agent first prepared in 1921 by Ott. It is prepared by slowly adding pure, finely powdered cyanuric chloride to an aqueous solution of a slight excess of sodium azide, and allowing the mixture to stand for a number of hours. The solid product is caught on a filter and washed well with water.

Cyanuric triazide forms colorless crystals, which melt at 94°C. and decompose when heated above 100°C. It detonates when heated rapidly or exposed to a flame. While insoluble in cold water, cyanuric triazide is readily soluble in hot ethyl alcohol, acetone, benzene, or ether and may be purified by recrystallization. However, this is to be avoided, as the relatively large crystals formed on recrystallization or by melting and cooling the compound are dangerously sensitive and detonate upon simple fracture.

The crystals of cyanuric triazide produced by the above method are very much more sensitive to impact and friction than mercury fulminate. It has a rate of detonation of 5545 m./sec. at density of only 1.15, and has brisance essentially that of TNT and DDNP as measured by the sand test. It does not decompose below 100°C., and this indicates satisfactory stability; but, it is slightly volatile and is more hygroscopic than mercury fulminate. It is a more efficient initiator of detonation than lead azide, as it will detonate ammonium picrate; it appears to be superior to DDNP in this respect.

Because of its hygroscopicity, volatility, and great sensitivity to impact, and the difficulty of controlling crystal size and, therefore, sensitivity, cyanuric triazide has not been used commercially or in ammunition so far as is known. It should be prepared only in very small quantities and handled with great care.

**Lead styphnate or 2,4,6-trinitroresorcinate (III)**, formula weight 450.30, is a relatively poor initiating agent, but because of its ease of ignition it is used to some extent as a cover charge for lead azide and as an ingredient of priming compositions.

The addition of a solution of sodium or magnesium styphnate to a solution of lead acetate results in the precipitation of a basic lead styphnate, which has relatively little explosive value. This may be converted into the normal salt by treatment with dilute nitric acid. The normal salt, first prepared by von Herz, can be obtained also by treating a solution of lead nitrate with a solution of sodium styphnate in the presence of acetic acid.

Normal lead styphnate is a finely divided, rhombic material of light orange or reddish-brown color, which crystallizes with half a molecule of water of crystallization. It has a crystal density of 3.02 and an apparent density varying from 1.0 to 1.6. It is insoluble or nearly so in water (0.04 gram/100 grams) and the common organic solvents. It can, therefore, be stored under water or a mixture of water and an alcohol. It is hygroscopic only to the extent of 0.05%. Lead styphnate apparently is un-

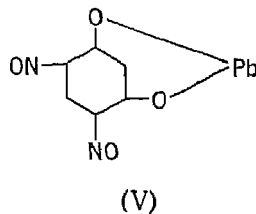
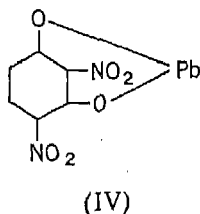
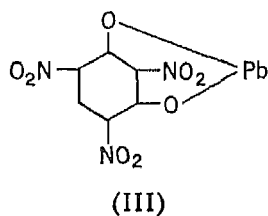
affected by sodium or ammonium hydroxide, but is decomposed by concentrated sulfuric or nitric acid.

When brought into contact with a flame or subjected to impact, lead styphnate explodes with a loud report. It has been reported to have rates of detonation of 4900 and 5200 m./sec. at densities of 2.6 and 2.9, respectively. Lead styphnate is less sensitive to impact and friction than mercury fulminate or amorphous lead azide, but is more sensitive to heat than lead azide. When subjected to the sand test with ignition by a black powder fuse, 10.5 grams of sand are crushed (Table III), but when a cover charge of lead azide is used, 24.0 grams of sand are crushed. Evidently the sensitivity of lead styphnate is such that its brisance and rate of detonation are determined by the manner in which it is initiated. Lead dinitroresorcinate, Tetracene, and nitrogen sulfide,  $N_4S_4$ , have also been found to yield varying brisance values with change in manner of initiation.

The stability of lead styphnate is excellent as judged by the 100°C. vacuum stability test, but the 100°C. heat test indicates it to be somewhat volatile at that temperature. That the compound is of a high order of stability is shown by its failure to show any significant change in ignitibility, stability, or brisance during storage at 80°C. for 8 weeks.

Lead styphnate has been found incapable of initiating the detonation of TNT or Tetryl but can cause the detonation of unpressed PETN. It will initiate straight 40% dynamite, but nonuniformity of initiation results when it is applied to gelatin dynamite.

These limitations have restricted the application of lead styphnate as an initiator, but it is used to some extent as a cover charge for lead azide, as a primary initiator caused to function by a bridge wire, and in priming compositions required to have certain blast characteristics.



**Lead dinitroresorcinate**, formula weight 405.30, as would be expected, is an even less powerful explosive and less efficient initiator than lead styphnate. The 2,4-dinitro compound (IV) is the one most frequently used. It has been found to be unusually sensitive to friction or stab action without being unduly sensitive to impact; therefore, it is particularly suitable for use as a priming material. It is prepared by treating lead nitrate in hot aqueous solution with a boiling solution of dinitroresorcinol to which the stoichiometric quantity of sodium carbonate has been added. After being cooled, the precipitated dinitroresorcinate is washed with water, alcohol, and ether before being dried.

When lead dinitroresorcinate is subjected to contact with a flame, it deflagrates but does not explode with the violence of lead styphnate. It is of the same order of sensitivity to impact as lead azide, but is much more sensitive to ignition. When subjected to the sand test with ignition by a black powder fuse, it crushes only 1.6 grams of



TABLE III. Test Data for Initial Detonating Agents.

Agent	Impact tests			Temp., min., °C. to cause explosion in:		Sand test, grains <sup>c</sup>	100°C. heat test, % loss in:		100°C. vacuum stability test, ml. <sup>d</sup>	75°C. international test, % loss in 48 hr.
	Test A, in. <sup>a</sup>	Test B, cm. <sup>a</sup>	Test C, cm. <sup>b</sup>	0.1 sec.	5 sec.		1st 48 hr.	2nd 48 hr.		
Mercury fulminate.....	2	5	24	263	210	22.1	Explodes	—	—	0.18
Silver fulminate.....	—	—	38	245	170	22.4	—	—	—	—
Lead azide, crystalline.....	—	—	43	383	345	17.6	—	—	—	—
Lead azide, dextrinated.....	5	11	—	396	325	16.7	0.5	0.1	0.2	0.17
Silver azide.....	3	6	41	308	290	24.2	—	—	—	—
Cyanuric triazide.....	—	—	7	252	—	39.2	—	—	—	—
DDNP.....	2	5	—	220	180	45.6	0.3	0.4	7.0	0.24
Lead styphnate.....	3	8	50	293	265	10.5	1.5	1.5	0.2	—
Lead dinitroresorcinate.....	4	—	—	—	265	1.6	0.2	0.02	< 0.4	0.34
Lead dinitrosorsorcinate.....	—	68	—	274	201	0.0	2.43	0.15	—	1.78
Tetracene.....	2	—	—	—	154	2.0	23.2	3.4	—	0.47
HMTD.....	—	—	8	200	< 149	39.0	—	—	—	—
Nitrogen sulfide.....	< 3	20	—	—	205	15.0	—	—	1.6 <sup>e</sup>	0.05

<sup>a</sup> Minimum height of fall of 2-kg. weight to cause an explosion in 10 trials.<sup>b</sup> Minimum height of fall of 1-kg. weight to cause an explosion in 10 trials.<sup>c</sup> Grams of sand crushed by 0.4 gram of explosive.<sup>d</sup> Ml. gas liberated by a 1.0-gram sample in 40 hours.<sup>e</sup> At 120 °C.

sand, but if primed with mercury fulminate it crushes ten times as much sand (Table III). Nothing is known of its rate of detonation. It is of the same order of stability as lead styphnate but is less volatile at 100°C.

The relative difficulty involved in the manufacture of lead dinitrosoresorcinate and the necessary control of crystal size and form has prevented the extensive use of the material at present; however, it has been found to be suitable for special designs of ammunition.

**Lead dinitrosoresorcinate** (probably the 4,6-isomer shown in formula V), formula weight 373.30, is an even weaker explosive than the dinitro salt of lead. It has been used since only about 1940. It is prepared from dinitrosoresorcinol by a method similar to that used for the preparation of normal lead styphnate. A basic salt can be formed by modifying the conditions of preparation.

Lead dinitrosoresorcinate is less sensitive to impact than Tetryl, and it has no brisance when ignited by a flame (Table III), as it undergoes deflagration only. When primed with mercury fulminate, it crushes only 3 grams of sand in the sand test. The stability of the material is distinctly less than that of lead styphnate, as it explodes in less than 2 hours in the 120°C. vacuum stability test and undergoes significant deterioration when stored at 80°C. for 10 days.

The practical value of lead dinitrosoresorcinate is found in its low ignition temperature, which is essentially that of mercury fulminate. This characteristic and its mild explosive action render it suitable for cover charges or priming compositions to be ignited electrically or by a black powder fuse.

**Miscellaneous Initiators.** A number of other compounds have been considered for practical use as initiators of detonation but have not been applied. These may be mentioned briefly. **Nitrogen sulfide** (sulfur nitride),  $N_4S_4$ , formula weight 184.27, has acceptable initiating, sensitivity, brisance, and stability characteristics. However, it offers no distinct advantage in any direction over the initiating agents now used for commercial or military purposes. **Hexamethylenetriperoxide diamine**

(HMTD) (*Ring Index* No. 1190),  $\text{CH}_2\text{O.O.CH}_2\text{N.CH}_2\text{O.O.CH}_2\text{N.CH}_2\text{O.O.CH}_2$ , formula weight

208.17, has excellent initiating, sensitivity, and brisance characteristics. However, it is unstable at ordinary temperatures in the presence of even atmospheric moisture and so is not suitable for practical use. **Lead picrate** or **trinitrophenolate**,  $((\text{NO}_2)_3\text{C}_6\text{H}_2\text{O})_2\text{Pb}$ , formula weight 567.41, is extremely sensitive to impact and is considered too dangerous for practical use. **Lead dinitrophenolate**,  $((\text{NO}_2)_2\text{C}_6\text{H}_3\text{O})_2\text{Pb}$ , formula weight 509.41, is too insensitive and has no initiating value and but little brisance when ignited with a flame. **1,3,5-Triazido-2,4,6-trinitrobenzene**,  $\text{C}_6(\text{N}_3)_3(\text{NO}_2)_3$ , formula weight 336.16, is of high initiating value and of acceptable sensitivity to impact, but is inherently unstable. It decomposes to the extent of 0.665% in 3 years at 20°C., and so cannot be considered suitable for practical use. **Mercurous azide**,  $\text{HgN}_3$ , formula weight 242.63, is of the same order of sensitivity as lead picrate, while mercuric azide,  $\text{Hg}(\text{N}_3)_2$ , formula weight 284.66, is so sensitive and unstable that it frequently undergoes spontaneous explosion during crystallization or at the slightest touch.

### Noninitiating High Explosives

The noninitiating high explosives comprise a considerable number of organic and inorganic chemical compounds, which are used in the formulation of binary explosives (see p. 56), plastic explosives (see p. 58), and blasting explosives (see p. 60).

**Binary explosives** are those obtained by mixing TNT and another explosive with or without a nonexplosive material. Binary explosives are designed primarily to be suitable for melt-loading into shell and bombs and are used only for military purposes.

*Plastic explosives* are mixtures of one or more high-explosive compounds with materials capable of forming plastic masses, which can be press-loaded or formed by hand. They are generally used for military demolition purposes.

There are hundreds of explosive compounds known, but only a few can be used practically because of the difficult requirements with respect to sensitivity, brisance, stability, nonvolatility, hygroscopicity, reactivity, cost, availability, etc. Only those compounds that have found practical application or are of special interest are discussed here.

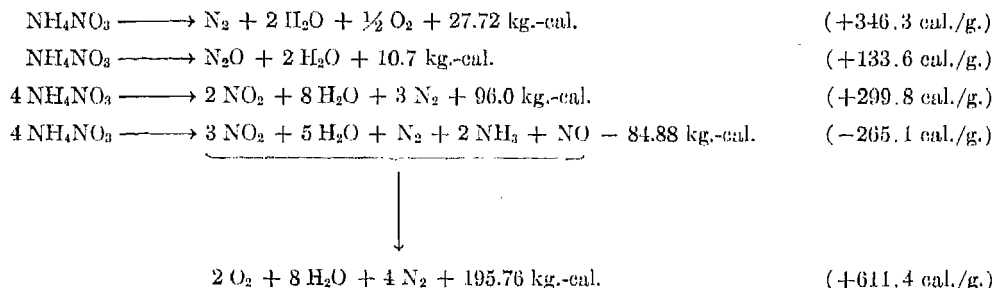
#### SINGLE-COMPOUND HIGH EXPLOSIVES

These may be divided into inorganic and organic compounds, with ammonium nitrate as the only important inorganic high explosive. The organic high-explosive compounds are of the aliphatic, aromatic, and heterocyclic series and include nitro compounds, nitramines, and nitrates. The aliphatic nitrates such as nitroglycerin and nitrocellulose were the first to achieve practical importance. Later the aromatic nitro compounds such as TNT and picric acid became of major military importance. It is only recently that the heterocyclic nitramine Cyclonite has achieved this status. These changes in direction of development reflect the early industrial availability of raw materials such as glycerin, cellulose, and sugars, the later appearance of coal-tar products such as toluene and phenol, and the relatively recent production in bulk of synthetic raw materials such as ammonia and formaldehyde.

**Ammonium nitrate**,  $\text{NH}_4\text{NO}_3$  (see Vol. I, p. 817), formula weight 80.05, has found wide application as an ingredient of blasting explosives, propellants, and shell and bomb bursting charges, as well as peacetime use as a fertilizer. Although first prepared by Glauber in 1659, it was not until 1867 that it was used as an explosive, when it was used by Ohlsson and Norrbom in what was essentially a dynamite.

Being overbalanced with respect to oxygen content, ammonium nitrate has no heat of combustion. Its heat of formation has been found to be 1098.46 cal./gram or 87.93 kg.-cal./mole at constant pressure.

On being heated, ammonium nitrate can undergo decomposition in a number of ways, depending upon the conditions of heating. The most important of these are:



These different modes of decomposition and thermochemical effects are of some practical importance in view of the insensitivity of ammonium nitrate to detonation.

Ammonium nitrate to be used as an ingredient of dynamites is in many cases coated with approximately 1% of waxy material such as a mixture of petrolatum, rosin, and paraffin. This is accomplished by adding the melted wax to the nitrate in the graining kettle (see under "Batch process," Vol. I, p. 821) when the temperature has decreased to within 5°C. of the discharge temperature. In some cases no wax coating

is used, but 0.3% of calcium carbonate is added during the graining operation. Anti-setting agents such as kieselguhr, fuller's earth, kaolin, zinc oxide, or special organic compounds sometimes are added instead of wax.

Ammonium nitrate of the grade used for the manufacture of military explosives is required to be at least 99.0% pure, contain not more than 0.02% free nitric acid, 0.05% sulfate, 0.18% water-insoluble material, 0.10% ether-insoluble material, and 0.50% chlorides, and be free from alkalinity and nitrites. The commercial grade used for the manufacture of dynamite is of comparable purity.

The nitrate content may be determined by treating a weighed sample with an excess of neutral formaldehyde solution at 60°C., cooling, and titrating with sodium hydroxide in the presence of phenolphthalein indicator. Correction must be made for any ammonium sulfate and chloride present. Purity may be determined also by means of a nitrometer, in which case no such correction need be made. An aqueous solution is tested for nitrite by means of a 0.5% solution of *m*-phenylenediamine hydrochloride in the presence of 0.1 gram sulfuric acid. Acidity is tested for by means of methyl red indicator.

Ammonium nitrate is an explosive of such low sensitivity that complete detonation of the pure material is difficult (Table IX). Its sensitivity to impact (P.A. machine) is so much less (impact test value, 31 in.) than that of ammonium picrate (17 in.), that it is essentially nonhazardous from this viewpoint. It is not sensitive to friction or rifle bullet impact and does not explode in the explosion temperature test. In the sand test it can be detonated only partially even when subjected to the action of a booster charge of Cyclonite or Tetryl. In larger quantities, when properly confined, it can be detonated by a booster charge of Tetryl, but not by a blasting cap containing lead azide or mercury fulminate. The sensitivity of ammonium nitrate to initiation decreases with increase in loading density. If the density exceeds 0.9, charges of 1 to 3 lb. cannot be detonated completely by large booster charges, and larger quantities cannot be detonated completely at a density exceeding 1.1.

While the admixture of up to 8% of carbonaceous material sensitizes ammonium nitrate, such mixtures also decrease in sensitivity with increase in density. Formerly it was thought that ammonium nitrate could not be caused to undergo detonation by the application of heat alone, but it has been found that this can be accomplished when the nitrate is subjected to confinement and a certain minimal gas pressure. The sensitivity of ammonium nitrate to impact increases somewhat with temperature:

Temperature, °C.....	25	75	100	150	175 (molten)
Impact test (2-kg. wt.), in.....	31	28	27	27	12

When molten it is approximately as sensitive as crystalline TNT at ordinary temperatures.

The rate of detonation of ammonium nitrate varies from 1100 to 2700 m./sec., depending upon the particle size, apparent density, degree of confinement, and efficiency of the initiating charge. The molten material, with little confinement of a 1.25 in. diameter charge, has been found to have a rate of detonation within the above range. Increase in the temperature of the charge from 15 to 140°C. has been found to result in an increase of 400 m./sec. in the rate of detonation. The detonation wave in ammonium nitrate tends to decrease in rate as it proceeds, and the distance of propagation depends upon the degree of confinement and the rate of the initiating

wave. Some investigators have claimed better initiation of ammonium nitrate by low-rate boosters than those like Tetryl and TNT.

With a low rate of detonation, ammonium nitrate would be expected to have correspondingly low brisance. It is too insensitive to undergo complete detonation in the sand test, but fragmentation tests of equal weights of ammonium nitrate and TNT at a density of 1.0 have shown the nitrate to produce only 24% as many fragments as TNT. Lead cylinder compression tests have indicated it to have approximately 55% of the effect of TNT. Trauzl lead block test values indicate ammonium nitrate to have 55% of the explosive power of TNT, but the heat of explosion values show the nitrate to have only 37% of the energy of TNT (Table X).

At ordinary temperatures ammonium nitrate is a very stable material (Table XI). It has been heated at 100°C. for 100 days without appreciable decomposition. It is slightly volatile at higher temperatures, but its 150°C. vacuum stability test value (0.3 ml. in 40 hours) shows it to be quite stable at even that temperature. Decomposition does not appear to begin until the compound melts. At 220°C. nitrous oxide, water, and nitrogen are formed. If an organic material such as cellulose is present, decomposition begins at 100°C. and is pronounced at 120°C., but other organic materials such as rosin have much less effect in this direction.

Ammonium nitrate is not toxic and the handling of it does not require special precautions from this viewpoint. It is a fire hazard in that it is a powerful oxidizing agent and will increase the spread and intensity of combustion of any flammable material mixed with or adjacent to it.

**Tetranitromethane** (Tetan),  $C(NO_2)_4$ , formula weight 196.04, in the pure state is a colorless liquid, which is quite volatile, has a lacrimatory effect and unpleasant taste, and is very toxic. It has had limited application as an ingredient of mixtures and as a material for the high-temperature cutting of metals; the use of such mixtures as explosives has been proposed. The compound was first prepared in 1861 by Schischkow, and is produced to a slight extent during the nitration of toluene to TNT by rupture of the benzene ring.

Pure tetranitromethane has the following constants: f.p., 14.2°C.; b.p., 125.7°C.;  $d_{15.8}^{16.8}$ , 1.6501;  $n_{D_0}^{16.9}$ , 1.43976; vapor pressure at 40°C., 25 mm. Hg; volatility at 60°C., 106 mg./sq.cm./hr.; heat of combustion, 457 cal./gram. It is insoluble in water, but is soluble in ether, ethyl alcohol, acetone, toluene, nitrobenzene, and nitrotoluene.

Because it contains a large excess of oxygen over that required for oxidation of its carbon, tetranitromethane can act as a powerful oxidizing agent. It can be steam-distilled, but undergoes some hydrolysis even at ordinary temperatures when in contact with water. The product of hydrolysis is trinitromethane (nitroform). Tetranitromethane reacts readily with aqueous potassium hydroxide to form the potassium salt of trinitromethane. It is reduced to guanidine by the action of iron or zinc and dilute hydrochloric acid. Reduction in moist ethereal solution with aluminum amalgam results in the formation of nitrogen, ammonia, and methylamine.

Tetranitromethane is prepared most easily by the action of fuming nitric acid on acetic anhydride, the other products being carbon dioxide and acetic acid: 300 ml. of ice-cold, colorless, fuming nitric acid (sp.gr. 1.52-1.53, produced by distilling a mixture of fuming nitric acid and 95% sulfuric acid under a pressure of 20 mm. of mercury) is placed in a flask containing glass chips and equipped with a stirrer, thermometer, condenser, and dropping funnel. The flask is placed in a bath packed with ice, and 650 ml. of commercial acetic anhydride is added slowly so that the temperature of the mixture is maintained at 15-20°C. After the mixture has stood at 25°C. for about 2 weeks, 3 liters of cold water is added and the oily bottom layer is separated. The aqueous layer is steam-distilled

and the oily bottom layer in the distillate is separated and added to the first fraction separated. The crude tetranitromethane is washed with a cold 5% sodium carbonate solution and then with cold water until free from carbonate. The washed product is dried over anhydrous sodium sulfate. The yield is 60-65% of the theoretical.

There are no commercial or military grades of tetranitromethane. The quality of the material can be judged by its freezing point, density, and degree of acidity.

As an explosive per se, tetranitromethane is of little value. Impact tests show it to be less sensitive than nitroglycerin, and this is confirmed by pendulum friction tests. In the explosion temperature test it undergoes decomposition without explosion in 5 sec. (Table IX), and even at 500°C. it does not detonate. Unless highly confined, tetranitromethane is difficult to initiate to detonation, but when so confined it detonates at a rate of 6400 m./sec. (Table X). Because of this insensitivity and because of the poor confinement in the tests, the sand test and Trauzl lead block test values of tetranitromethane are unduly low and not representative. Fragmentation tests have shown tetranitromethane to produce 80% as many fragments as nitroglycerin, which is approximately the relationship between their rates of detonation.

Pure tetranitromethane is thermally stable. When 2.5-gram samples of it and nitroglycerin were heated at 90°C. for 6 hours in a special manometric apparatus, the nitroglycerin evolved 1.6 ml. of gas while the tetranitromethane liberated none. However, tetranitromethane is quite unstable in the presence of even atmospheric moisture, as even the purified and dried material at 20°C. produces a blue coloration of potassium iodide-starch paper in less than 1 minute when the paper is suspended in the air over the tetranitromethane. This indicates the rapid formation of at least traces of free acid.

Tetranitromethane is of interest chiefly as an ingredient of liquid explosives formed by mixing the compound with a liquid fuel such as toluene, nitrobenzene, or nitrotoluene. Such mixtures are extremely powerful explosives but are apt to be very hazardous. It is recorded that the explosion in a laboratory of 15 grams of a tetranitromethane-toluene mixture killed 10 and injured 20 persons. These mixtures become increasingly sensitive and powerful as they approach those representing oxygen balance of the ingredients.

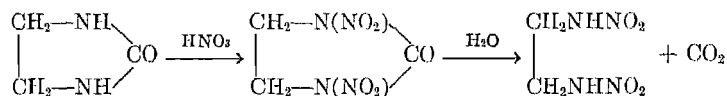
The toxicity of tetranitromethane is pronounced. The vapors have an irritating action on the mucous membranes of the eyes and nose, and inhalation causes extreme edema of the lungs. Cats exposed to air containing 7-25 p.p.m. tetranitromethane died within 4 to 6 hours, and the fatality of certain cases of "TNT-poisoning" has been ascribed to the presence of tetranitromethane. The maximum allowable concentration in air may be as low as 1 p.p.m.

**Ethylenedinitramine** (*N,N'*-dinitroethylenediamine (*C.A.*), Haleite, EDNA),  $\text{NO}_2\text{NHCH}_2\text{CH}_2\text{NHNO}_2$ , formula weight 150.10, is a white, orthorhombic, crystalline solid. It has been standardized for military use in the U.S. under the name of Haleite. The compound was first described by Franchimont and Klobbie in 1887.

Ethylenedinitramine has the following constants: m.p., 177.3°C. (dec.); sp.gr., 1.75;  $n_D^{20}$  (of crystals obtained from alcohol),  $\alpha = 1.427$ ,  $\beta = 1.686$ , and  $\gamma = 1.730$ ; heat of combustion ( $\Delta H_v$ ), 2506 cal./gram. Ethylenedinitramine is soluble to the extent of 0.3, 1.25, 4.95, and 16.4 grams/100 grams water at 25, 50, 75, and 95°C., respectively, but its hygroscopicity is only 0.01%. It is soluble to the extent of 1.25, 3.45, and 10.1 grams/100 grams ethyl alcohol (95%) at 25, 50, and 75°C., respectively. It is insoluble in ether, but soluble in nitrobenzene and dioxane.

A solution of ethylenedinitramine in water is slightly acid, and it forms neutral lead, silver, and potassium salts by replacement of the *N*-hydrogen atoms with metal. On treatment with hot, dilute sulfuric acid, ethylenedinitramine decomposes with the formation of nitrous oxide, acetaldehyde, and glycol.

Ethylenedinitramine is obtained by nitrating 1,3-ethyleneurea (2-imidazolidone (*C.A.*)), which is prepared from ethylenediamine and diethyl carbonate, and hydrolyzing the dinitroethyleneurea:



Ten parts by weight of mixed acid (74.0% sulfuric acid, 15.4% nitric acid, and 10.6% water) is cooled to 10°C. or less and agitated, and 1 part of ethyleneurea is added in small portions at such a rate that the temperature does not rise above 10°C. Stirring is continued for 5 minutes after the addition of the last portion of ethyleneurea. The resulting solution is poured into a large volume of ice water and the precipitated dinitroethyleneurea is caught on a filter and washed well with water. The dinitro compound is suspended in water, which is heated to boiling. Boiling is continued until the evolution of gas ceases. When the solution is cooled to room temperature, the ethylenedinitramine separates as shining crystals. These are caught on a filter, washed with cold water, and dried.

The standard grade of ethylenedinitramine is required to have a minimum purity and melting point of 94.0% and 174.0°C., respectively. Material having a purity of 99.6% or more has been found to have a melting point of at least 176.5°C. and to evolve less than 1.0 ml. of gas in the 100°C. vacuum stability test. Purity is determined by treating a weighed sample with an excess of boiling *N*/3 sodium hydroxide solution, which forms the disodium salt, cooling, and titrating the excess hydroxide with sulfuric acid solution, using phenolphthalein as the indicator.

As an explosive, ethylenedinitramine has somewhat unusual characteristics. Although it has a higher rate of detonation than Tetryl at the same density and essentially the same brisance, as judged by the sand test (Table X), ethylenedinitramine is distinctly less sensitive to impact and slightly less sensitive to friction and initiation by lead azide or mercury fulminate (Table IX). As indicated by ballistic pendulum tests, ethylenedinitramine is slightly more powerful than Tetryl; it also has a higher heat of explosion value than Tetryl. Although ethylenedinitramine has a much lower explosion temperature test value than Tetryl, the pure explosives are of the same order of stability as judged by vacuum stability test values (Table XI). Ethylenedinitramine has been found to withstand storage at 50°C. When heated with boiling water, it slowly undergoes partial hydrolysis.

Ethylenedinitramine is not particularly toxic and no special precautions are required in connection with its manufacture and handling.

The lead salt of ethylenedinitramine is of the same order of sensitivity to impact as mercury fulminate, but it cannot be detonated by flame or stab action. It therefore is not suitable for use in blasting caps or detonators. The lead and the silver salts are insoluble in water, but the sodium and the potassium salts are readily soluble in water.

**Nitroguanidine** (see *Guanidine*),  $\text{HN:C(NH}_2\text{)NHNO}_2$ , formula weight 104.07, exists in two crystal forms having the same melting point. The  $\alpha$ -form or flat-needle form is that usually produced. The  $\beta$ -form, obtained in clusters of plates, can be transformed into the  $\alpha$ -form by dissolving it in sulfuric acid and pouring it into water. Neither form can be converted into the other by solution in water, and the two forms can be separated from each other by fractional crystallization from water. The com-

pound has found some use in propellants and trench mortar shell charges. It was first prepared in 1877 by Jousselin.

Nitroguanidine is a white crystalline solid having a crystal density of 1.715. The melting point varies somewhat with the rate of heating, but when this is moderate the pure material melts at 232°C. Its heat of combustion ( $\Delta H_p$ ) is 1997 cal./gram. The two forms differ slightly with respect to solubility in water but are similar at 25 and 100°C., where the solubility is about 0.44 and 8.25 grams/100 grams water, respectively. However, the compound is nonhygroscopic. Nitroguanidine is insoluble in ether and only very slightly soluble in ethyl alcohol, methanol, or acetone. Nitroguanidine is somewhat soluble in sulfuric acid, the solubility increasing with increase in concentration. In 45% sulfuric acid, nitroguanidine is soluble to the extent of 5.8 and 10.9 grams/100 ml. acid at 0 and 25°C., respectively.

On reduction, nitroguanidine is converted first into nitrosoguanidine and then into aminoguanidine:



Upon solution in hot, concentrated nitric acid, nitroguanidine yields a nitrate, which melts at 147°C. with decomposition. Nitroguanidine gives a blue color with diphenylamine reagent. In sulfuric acid solution, nitroguanidine acts as if it had decomposed into nitramide and cyanamide. When the solution is warmed, first nitrous oxide and some nitrogen are evolved and then carbon dioxide. At a more elevated temperature, ammonia and carbon dioxide are evolved. Upon treatment with ammonium carbonate, nitroguanidine yields guanidine carbonate.

Nitroguanidine is prepared by the dehydration of guanidine nitrate with sulfuric acid. The guanidine nitrate may be prepared by the reaction of guanidine and nitric acid or that of dicyanamide and ammonium nitrate. To effect the dehydration of guanidine nitrate, 500 ml. of concentrated sulfuric acid (95%) is cooled with ice and 400 grams of dry guanidine nitrate is added in small portions with stirring, so that the temperatures does not rise above 10°C. As soon as all the crystals have been dissolved, the milky liquid is poured into 3 liters of cracked ice and water. The mixture is kept ice-cold until precipitation is complete. The nitroguanidine is caught in a filter, washed with water, and recrystallized from water. The yield is approximately 90% of the theoretical.

As guanidine nitrate can be produced from the raw materials coke, limestone, atmospheric nitrogen, and water, the production of nitroguanidine does not involve the availability of special natural resources such as petroleum or the by-product of an industry such as coke-industry toluene.

The standard military grade of nitroguanidine is at least 99.5% pure and contains not more than 0.20% water-insoluble material, 0.06% acid, and 0.30% ash. Purity is determined by means of a nitrometer. Acidity is determined by titration with standard alkali, using phenolphthalein as the indicator.

With an impact test value of 47 cm. (Table IX), nitroguanidine is distinctly less sensitive than Tetryl. Like TNT, it is not detonated in the rifle bullet impact test. It is less sensitive to initiation than TNT, as it cannot be initiated by mercury fulminate alone in the sand test and requires a minimum detonating charge of 0.72 gram of DDNP as compared with 0.29 gram for TNT. Nitroguanidine in larger amounts can be detonated by means of a blasting cap. At a density of 1.55, it has a rate of detonation of 7650 m./sec. as compared with rates of 7300 and 6800 for Tetryl and TNT, respectively, at the same density. The brisance of nitroguanidine, however, is less



than that of TNT as judged by the sand test and its power is only 104% that of TNT as measured by the ballistic pendulum test (Table X).

Nitroguanidine is very stable as judged by vacuum stability test values (Table XI), having the same order of stability as TNT and being somewhat more stable than Tetryl. Its explosion temperature test value of 275°C. is only slightly greater than that of Tetryl.

Because it is not of outstanding brisance or power, nitroguanidine has had only limited application as an explosive. Its high nitrogen content and the relatively low temperature developed by its explosion (approximately 2100°C.) render nitroguanidine of interest for use in compositions having low-temperature, nonflashing characteristics.

**Glycol dinitrate** (ethylene nitrate, ethylene glycol dinitrate, nitroglycol, GDN) (see *Glycols*),  $\text{NO}_3\text{CH}_2\text{CH}_2\text{NO}_3$ , formula weight 152.07, is a colorless liquid at ordinary temperatures. It is used to a certain extent in the manufacture of low-freezing dynamites. It was first prepared by Henry in 1870, but was not used commercially until much later because of the high cost of ethylene glycol as compared with that of glycerin.

Glycol dinitrate has the following constants: f.p.,  $-22.8^\circ\text{C}.$ ;  $b_2$ ,  $70^\circ\text{C}.$ ;  $b_{50}$ ,  $125^\circ\text{C}.$ ;  $d_{20}^{20}$ , 1.489;  $n_D^{20}$ , 1.4470; vapor pressure, 0.05 mm. Hg at  $20^\circ\text{C}.$ , 1.4 at  $60^\circ\text{C}.$ ; volatility at  $60^\circ\text{C}.$ , 2.20 mg./sq.cm./hr.; viscosity at  $20^\circ\text{C}.$ , 4.2 centipoises; heat of combustion ( $\Delta H_p$ ), 1753 cal./gram; ignition temperature at atm. pressure, 195–200°C. Glycol dinitrate is comparable with nitroglycerin with respect to solubility in organic solvents and solvent power, but it is more soluble in water (0.52 and 0.85 gram/100 grams water at 25 and  $60^\circ\text{C}.$ ). It is an even better colloidizing agent for nitrocellulose than is nitroglycerin, since it acts at ordinary temperatures while nitroglycerin requires a slightly elevated temperature for such action.

The chemical reactivity of glycol dinitrate also is comparable with that of nitroglycerin. Because of its greater solubility in water, glycol dinitrate is slightly more susceptible to hydrolysis than nitroglycerin (0.008 and 0.005%, respectively, in 5 days at  $60^\circ\text{C}.$ ). Glycol dinitrate can be manufactured with the same apparatus and mixed acid used for the manufacture of nitroglycerin (see p. 28). The nitration can be carried out at a lower temperature because glycol is less viscous than glycerin. Less compressed-air agitation and washing with water are used because of the fact that glycol dinitrate is more volatile and more soluble in water than nitroglycerin. Most of the glycol dinitrate produced is in the form of a mixture with nitroglycerin obtained by nitrating a mixture of glycol and glycerin.

One of the very few exactly oxygen-balanced explosives, glycol dinitrate resembles nitroglycerin with respect to its burning and explosion characteristics, but is slightly less prone to explosion through burning. Impact and pendulum friction test values (Table IX) show that glycol dinitrate is much less sensitive than nitroglycerin to impact and friction, but it must be classified as a hazardous explosive. It is less sensitive than nitroglycerin to explosion by heat as indicated by their explosion temperature test values.

Glycol dinitrate has very high brisance as indicated by the sand test (Table X), its value being as great as that for any other single-ingredient explosive. The fact that glycol dinitrate has a lower rate of detonation than nitroglycerin must be attributed to the lower density of glycol dinitrate. Like nitroglycerin, glycol dinitrate can detonate at high and low rates—7300 and 2000 m./sec. Glycol dinitrate is more pow-

erful than any other single-ingredient explosive, as shown by Trauzl lead block test values reflecting the high heat of explosion, the highest of any of the explosives listed in Table X.

While the presence of more than slight traces of free acid renders glycol dinitrate unstable, vacuum stability test values (Table XI) show it to be much more stable than nitroglycerin. From its low 120°C. vacuum stability test value it may be concluded that glycol dinitrate is of the same order of thermal stability as Tetryl.

As in the case of nitroglycerin, the quality of glycol dinitrate is determined and controlled by control of the raw material from which it is manufactured. This is somewhat easier in the case of glycol than glycerin, as glycol is manufactured by synthetic methods whereas most of the glycerin produced is derived from animal fats. Tests of glycol dinitrate for quality and impurities are the same as those made of nitroglycerin.

Due to limited use and the hazards of handling, glycol dinitrate is never transported as such beyond the plant in which it is manufactured. Because of its greater volatility, inhalation of the vapors of glycol dinitrate is more difficult to avoid than in the case of nitroglycerin. The effects of the absorption of glycol dinitrate are dilation of the blood vessels, acceleration of heart action, and severe headache. It is thought that continued exposure may cause some organic impairment.

Although it is somewhat less hazardous with respect to shock than nitroglycerin, in the manufacture of glycol dinitrate the same types of equipment and precautions are used. The use of glycol dinitrate is limited by its volatility and sensitivity, and extension of its use beyond dynamite manufacture does not appear probable.

**Diethylene glycol dinitrate** (dinitrodiglycol, DEGN) (see *Glycols*),  $\text{NO}_2\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2\text{CH}_2\text{NO}_2$ , formula weight 196.12, is a colorless liquid, which, in cooling, solidifies to a stable form (m.p. 2°C.) or a labile form (m.p. -10.9°C.). Diethylene glycol dinitrate was used in propellant composition by the Germans during World War II, but has had no other practical application to date. It was first described in 1927 by Rinckenbach.

Pure diethylene glycol dinitrate has the following constants: b.p., 160°C. (when heated rapidly);  $d_{4}^{20}$ , 1.385;  $n_D^{20}$ , 1.4517; vapor pressure, 0.0036 mm. Hg at 20°C., 0.130 at 60°C.; volatility at 60°C., 0.19 mg./sq.cm./hr.; viscosity at 20°C., 8.1 centipoises; heat of combustion ( $\Delta H_p$ ), 2792 cal./gram. Diethylene glycol dinitrate is similar to nitroglycerin with respect to miscibility with and solubility in organic solvents and solvent action on organic materials. It is distinctly more soluble in water (0.40 and 0.46 gram/100 grams water at 25 and 60°C.) than is nitroglycerin, but less so than glycol dinitrate. It is an excellent colloidizing agent for nitrocellulose.

With respect to chemical reactivity, diethylene glycol dinitrate resembles nitroglycerin, but it is less subject to hydrolysis (0.003% at 60°C. in 5 days) in spite of its greater solubility in water, and it is not readily saponified by alcoholic sodium hydroxide.

Diethylene glycol dinitrate can be prepared by adding the glycol to mixed acid at temperatures as high as 30°C. The mixed acid composition is approximately 50.3% nitric acid, 44.7% sulfuric acid, and 5.0% water. The yield is approximately 85% of the theoretical, and the spent acid contains approximately 24.2% water, 60.8% sulfuric acid, 10.7% nitric acid, and 3.3% of the dinitrate. This spent acid is very unstable and "fumes off" if heated or allowed to stand for a few days. The recovery of the spent acid, therefore, is difficult. Another process of manufacture consists of adding, over a period of 40 minutes, 1 part by weight of diethylene glycol to 2.7 parts of mixed acid (70% nitric acid and 30% sulfuric acid) that has been cooled to a very low temperature. The final temper-

ature is not permitted to exceed 10°C. The separated nitrate is washed with water, a sodium carbonate solution, and water. The spent acid is stabilized by the addition of 20% of 98% sulfuric acid, which renders recovery practicable. The first wash water contains 30% of nitric acid, which is recovered separately.

Diethylene glycol dinitrate can be ignited only with difficulty, it being necessary to first heat the liquid somewhat above room temperature. When so ignited, it burns quietly with a yellow luminous flame. When a small quantity in a capillary tube is thrust into a gas flame, it does not detonate as does nitroglycerin, and vapor ejected from the end of the tube burns quietly.

While considerably less sensitive to impact than nitroglycerin or glycol dinitrate, diethylene glycol dinitrate is sufficiently sensitive to friction to explode in the pendulum friction test (Table IX). It is distinctly difficult to detonate. The brisance of diethylene glycol dinitrate is slightly less than that of TNT, as measured by the sand test, and only 82% that of nitroglycerin (Table X). Like nitroglycerin, it appears to be capable of detonating at two rates, these being 1800-2300 and 6800 m./sec. In power it is between TNT and nitroglycerin, as indicated by ballistic pendulum and Trauzl lead block test values.

Like other aliphatic nitrate esters, diethylene glycol dinitrate is decomposed by free acid. Vacuum stability test data (Table XI) indicate the pure compound to be of the same order of stability as glycol dinitrate and Tetryl. The quality of diethylene glycol dinitrate is dependent upon the purity of the diethylene glycol used for its preparation, the presence of ethylene glycol or a polyglycol resulting in the presence of the nitrated impurity. The methods of analysis used for testing nitroglycerin are applicable also to diethylene glycol dinitrate.

Inhalation of its vapors or absorption of liquid diethylene glycol dinitrate through the skin can cause the same effects as those produced by nitroglycerin, but there is some evidence that fewer individuals are so affected than in the case of nitroglycerin.

While diethylene glycol dinitrate has been used in propellant compositions, this has been in spite of undesirable volatility, which may limit its future use in this direction. As an ingredient of blasting explosives it is handicapped by greater difficulty of manufacture and the generally higher cost of the glycol as compared with glycerin.

**Nitroglycerin** (more correctly called glyceryl trinitrate) (see *Glycerol*),  $\text{NO}_2\text{CH}_2\text{CH}(\text{NO}_2)\text{CH}_2\text{NO}_2$ , formula weight 227.09, is a colorless liquid at ordinary temperatures. It freezes to form dipyramidal rhombic crystals of a stable form (m.p. 13.2°C.). Under some conditions it may freeze to yield triclinic crystals, which represent a labile form (m.p. 2.2°C.). Crystals of the labile form after a week or two gradually change into the stable form.

Nitroglycerin is used largely in the manufacture of dynamites and propellants, and finds limited application as a medicinal (U.S.P. XIII) since a dose of only 0.0006 gram causes dilation of the arteries. It was first prepared in 1846 or 1847 by Sobrero. However, it was not until 1864 that, through the inventions of Alfred Nobel, the compound assumed any practical importance. Nitroglycerin became the basis of the dynamite industry and may be considered the first high explosive from the viewpoint of practical application.

Pure nitroglycerin has the following constants: b.p., 145°C. (with violent decomposition);  $b_{75}$ , 125°C.;  $b_{60}$ , 180°C.;  $d_{15}^{20}$ , 1.596;  $n_D^{20}$ , 1.4732; vapor pressure, 0.0015 mm. Hg at 20°C., 0.060 at 60°C.; volatility at 60°C., 0.11 mg./sq.cm./hr.; viscosity at 20°C., 35.5 centipoises; heat of combustion ( $\Delta H_p$ ), 1622 cal./gram. Nitroglycerin

is miscible in all proportions with acetone, ethyl ether, glacial acetic acid, benzene, nitrobenzene, chloroform, ethylene dichloride, and methanol, but is soluble only to limited extents in ethyl alcohol, propyl alcohol, isopropyl alcohol, and amyl alcohol. It is soluble to the extent of only 0.14 and 0.24 gram/100 grams water at 25 and 60°C., respectively. Nitroglycerin has some solvent power for aliphatic nitrate and aromatic nitro compounds, but essentially none for inorganic nitrates. It is an excellent colloid agent for nitrocellulose.

Concentrated sulfuric acid dissolves nitroglycerin through decomposition with the liberation of nitric acid. The reaction between aqueous sodium hydroxide and nitroglycerin is very slow because of immiscibility of the two liquids, but if ethyl alcohol is added the reaction is rapid. The products are sodium nitrate, nitrite, formate, and acetate, as well as oxalic acid and ammonia. An aqueous solution of sodium sulfide decomposes nitroglycerin rapidly, and this reaction provides a practical method for the disposal of waste nitroglycerin.

Nitroglycerin is manufactured by adding slowly 1 part by weight of glycerin (approximately 700 lb.) to about 4.3 parts of a mixed acid, contained in an iron, steel, or lead nitrator. The anhydrous acid contains about 52.7% nitric acid, 49.4% sulfuric acid, and 0.35% nitrosylsulfuric acid. It is stirred constantly by means of compressed air and cooled by means of brine coils, the temperature being kept at 25°C. or less. Should control of the temperature be lost or red fumes be evolved, the charge is dumped into a large drowning tank full of water. After addition of the glycerin to the mixed acid is completed, the emulsion of nitroglycerin in water and acid is subjected to additional agitation and cooling until the temperature is about 15°C. The charge then is run into a separating tank, where the nitroglycerin forms a supernatant layer containing about 8% nitric and 2% sulfuric acids. Agitation of the nitroglycerin with water at a temperature as high as 43°C. (drowning wash) removes most of the dissolved acid. After settling out, the nitroglycerin is given additional washes with water, 2% sodium carbonate solution, and water until the wash waters are free from alkali and the nitroglycerin is neutral to litmus. The purified nitroglycerin, which appears milky because of the moisture content, is transferred to storage tanks in a heated building. Here it rapidly becomes colorless and the moisture content decreases to 0.4% or less. The yield of nitroglycerin is  $230 \pm 5$  parts by weight per 100 parts of glycerin.

The spent acid from the nitration of glycerin contains approximately 10% nitric acid and 73% sulfuric acid. This is subjected to processing for recovery of the nitric acid and concentration of the resulting dilute sulfuric acid (see *Nitration*).

In Europe the Schmid and Biazzi continuous processes for the production of nitroglycerin have been used.

**Schmid Process.** This continuous process for the nitration of glycerin and the purification of nitroglycerin was patented in 1927. It involves continuous nitration, separation of nitroglycerin from spent acid, and purification by neutralization and washing.

The nitrator used has a capacity of approximately 50 gal. and is equipped with a propeller, vertical cooling tubes, and an overflow exit. A two-way valve, which connects to the mixed-acid line or may be opened to the drowning tank, is fitted centrally to the bottom of the nitrator. A hollow cone is fixed somewhat above the outlet of the valve. Brine at -5°C. is circulated around the cooling tubes in the annular space outside the reaction chamber. As mixed acid is fed in from the bottom, glycerin is fed in from the top at a level below that of the overflow exit. The propeller mixes the two liquids, and this action is enhanced by aeration through the propeller shaft and blades. The mixture then passes through the cooling pipes at such a rate that the temperature at the overflow exit does not exceed 18°C.

The nitroglycerin-mixed acid mixture flows by gravity to an acid separator, which consists of a tilted rectangular tank containing baffles and equipped with a bottom draw-off valve for spent acid, a sight glass near the top, and a steel neck with overflow pipe for the nitroglycerin. The spent acid is discharged to the acid recovery plant, and the nitroglycerin flows by gravity to the base of the first of the washing columns. Each column is approximately 9 ft. from base to overflow and consists of superimposed glass rings separated by perforated steel plates and rubber ring gaskets. The bottom ring is sealed into a steel base equipped with inlet connections for low-pressure air, wash liquid, and

nitroglycerin. The top ring is fitted with a steel head provided with an overflow to an intermediate separator.

As the nitroglycerin from the separator enters the bottom of the first washing column, it is mixed with cold water and emulsified by means of air injected into the mixture. This also forces the material to rise to the top of the column, where it overflows into the intermediate separator, which discharges nitroglycerin by gravity to the bottom of the second washing column. Here, and in the third column, a cold 2.5% solution of sodium carbonate is used instead of water. The fourth column, located in a separate house, uses hot water, and the fifth column uses cold water. The nitroglycerin from the separator next to the fifth washing column is passed through a four-ply flannel filter bag before being caught in a lead tank for storage and use. The wash liquors are run through a series of cataract tanks. Any nitroglycerin held by these is drawn off periodically and rewashed.

**Biazzì Process.** This process for the nitration of glycerin was patented in 1935. It offers the advantage of greater safety than the Schmid process because of the smaller amount of nitroglycerin in the system at a given time. Only 25 to 75 lb. of separated nitroglycerin is present at any time when 1000 lb. of nitroglycerin is made in 1 hour in a 10-gal. Biazzì nitrator. The process has been used also for the production of glycol dinitrate and diethylene glycol dinitrate. The equipment for the Biazzì process is manufactured in Vevey, Switzerland.

The nitrator has helical instead of vertical cooling coils and is designed to permit rapid reaction through rapid heat absorption. Because of this, the mixed acid used for nitration is stronger than that used in the Schmid process.

In the separator, provision is made for slowly rotating the intermediate emulsion layer, with consequent improvement in the breaking of the emulsion, and prevention of local overheating and formation of "dead spots."

The stainless-steel washing tanks are of about half the size of the nitrator and utilize high-speed mechanical agitation instead of compressed air. Several washers are used in series, with the wash waters flowing countercurrent to the nitroglycerin when this is to be used in propellants. Nitroglycerin for dynamite is washed only once. Sodium carbonate solution is used as in the Schmid process. Nitroglycerin is washed completely in 10 minutes.

Spent acid from the nitrator flows continuously into a dilutor, where 2% of water is added to dissolve traces of suspended nitroglycerin. Automatic control devices are used to indicate if temperatures are too high or low, to cut off feeds if there is current or belt failure, and to drown the nitration mixture if the temperature exceeds a set limit. The process requires a minimum of space, a unit for 2500 lb. of nitroglycerin per hour being housed in a 500 sq.ft. building only 12 ft. high. Nitroglycerin produced by the Biazzì process is claimed to be of unusual purity and stability. Complete freedom from explosions during manufacture also is claimed for the process.

Unconfined nitroglycerin in very small quantity burns without explosion when ignited, but if the material is confined or the quantity is sufficient to permit local overheating, explosion results. It is of the same order of sensitivity to impact as dextrinated lead azide (Table IX) and very sensitive to frictional impact. The sensitivity to impact is increased markedly by increase in temperature, while the frozen solid is much less sensitive than the liquid. However, many accidents have occurred when frozen dynamite was jarred while being thawed, and this is attributed to nitroglycerin possibly being peculiarly sensitive while undergoing transition from the labile to the stable form. Nitroglycerin can be initiated to detonation, although not uniformly, even by a black powder squib; so, it is almost as sensitive to initiation as are lead azide, mercury fulminate, etc.

As measured by the sand test, the brisance value of nitroglycerin is one of the highest recorded (Table X), being almost as great as that of glycol dinitrate and slightly greater than those for solid explosives such as Tetryl and TNT. Nitroglycerin can undergo detonation at rates as low as 1500 to 2000 m./sec., but, when the diameter of the charge is not too small and a strong detonator is used, rates as high as 8500 m./sec. have been obtained. It may be considered that a value of 7700 m./sec. is representative of the upper rate of detonation of nitroglycerin. The power of nitroglycerin as

measured by the Trauzl lead block test (Table X), is almost as great as that of any known single-ingredient explosive. This reflects the high heat of explosion of the compound, which is exceeded only by that of glycol dinitrate.

The retention of more than slight traces of free acid renders nitroglycerin quite unstable, decomposition with the appearance of red fumes taking place in a few days. At temperatures below 50°C., pure nitroglycerin is of such stability that it withstands storage for years. However, the rate of acceleration of decomposition increases rapidly above 50°C., and at 145°C. decomposition is so rapid that the liquid appears to be boiling. In the explosion temperature test it explodes at 222°C. Vacuum stability test values (Table XI) show nitroglycerin to be much less stable than glycol dinitrate and solid explosives such as PETN, Tetryl, and TNT. Nitroglycerin is very slightly susceptible to hydrolysis (0.002% in 10 days at 22°C. and 0.005% in 5 days at 60°C.).

There are no standard commercial grades of nitroglycerin, the quality being determined and controlled by that of the glycerin used in manufacture. Glycerin used for the manufacture of dynamite nitroglycerin is purified by distillation so as to have a density of 1.262 or higher, a glycerin content of at least 99%, and a moisture content less than 1%. In the U.S., nitroglycerin for military purposes is required to contain not more than 0.002% free acid or alkali and have a nitrogen content not less than 18.40%. Acidity or alkalinity is determined by washing a benzene solution of the sample with water and titrating the water washes with sodium hydroxide or sulfuric acid solution, using methyl orange as the indicator. Nitrogen content is determined by means of a nitrometer, the nitrate nitrogen being converted into nitric oxide, the volume of which is measured.

Nitroglycerin as such is not transported by common carrier because of its sensitivity to shock. A 70-30 nitroglycerin-acetone mixture is relatively insensitive and sometimes is transported by wagons, trucks, etc. The nitroglycerin can be separated from the acetone by evaporating the latter with a current of air or by precipitating the nitroglycerin by the addition of an excess of water.

Nitroglycerin is readily absorbed through the skin into the circulatory system of the human body, and vapors inhaled into the lungs are similarly absorbed by the blood. The effect of such absorption is a severe and persistent headache. Workers in constant contact with the material soon develop an immunity to this effect, this immunity being maintained only by continued contact. Strong black coffee or caffeine citrate gives some relief to the sufferer from an "NG headache."

Nitroglycerin is the most hazardous explosive handled in relatively large quantities, and extreme precautions are observed in the course of its manufacture and use. Barricaded buildings, emergency drowning tanks, remote control of operations, rubber hose connections, rubber-tired transportation buggies, etc., are examples of these precautions.

The only uses for nitroglycerin as such are for the "blowing in" of oil wells and as a medicinal agent. In admixture with other materials, it is used in the manufacture of dynamites and propellant compositions.

**Diglycerin tetranitrate** (tetranitrodiglycerin),  $\text{NO}_2\text{CH}_2\text{CHNO}_2\text{CH}_2\text{OCH}_2\text{CHNO}_2\text{CH}_2\text{NO}_2$ , formula weight 346.17, is seldom prepared in the pure form, generally being formed by the nitration of a mixture of glycerin and diglycerin, which is obtained by heating glycerin. The presence of about 0.5% of sodium sulfite accelerates the condensation of glycerin to diglycerin. Mixtures of nitroglycerin and diglycerin tetra-

nitrate have long been used in the manufacture of low-freezing dynamites. It was first prepared in 1861 by Lourenzo.

Diglycerin tetranitrate is a very viscous liquid having a density of 1.33. It is insoluble in water but readily soluble in ether and ethyl alcohol. It is not as good a colloidizing agent as nitroglycerin for nitrocellulose. Markedly less sensitive than nitroglycerin to impact or initiation, diglycerin tetranitrate is about 85% as powerful, as indicated by Trauzl lead block tests.

**Erythritol tetranitrate** (nitrocrythrite),  $\text{NO}_3\text{CH}_2(\text{CHNO}_3)_2\text{CH}_2\text{NO}_3$ , formula weight 302.12, exists as colorless crystals (m.p.  $61.5^\circ\text{C}.$ ), which are insoluble in cold water but are soluble in alcohol and ether. It can be prepared by dissolving erythritol in strong nitric acid and adding sulfuric acid, which precipitates the tetranitrate from the nitric acid solution.

As an explosive, erythritol tetranitrate is one of the most powerful known, as it has a higher sand test value than nitroglycerin or PETN (Table X). It is only slightly inferior to glycol dinitrate as an explosive. It is of the same order of sensitivity to impact as nitroglycerin and has essentially the same explosion temperature test value (Table IX). It resembles nitroglycerin also with respect to stability as indicated by  $100^\circ\text{C}.$  vacuum stability test values (Table XI). It has a heat of combustion value of 1546 cal./gram. Unlike PETN, erythritol tetranitrate reduces Fehling solution.

Because of the rarity and cost of erythritol (see *Alcohols, higher polyhydric*), the tetranitrate has never been used as an explosive. It is of interest, however, as one of the series of polynitrate esters of aliphatic alcohols.

**Pentaerythritol tetranitrate** or **PETN** (nitropentaerythrite, pentrit),  $\text{C}(\text{CH}_2\text{NO}_3)_4$ , formula weight 316.15, forms colorless, nonhygroscopic, prismatic crystals. The compound has found use in detonating-fuse and priming compositions, as well as in composite explosives used in grenades, etc. The compound was first prepared in 1891 by Tollens, but it was not used on a practical basis until after World War I. It can be made by reacting formaldehyde and acetaldehyde to form pentaerythritol and nitrating this, and it offers certain logistic advantages in time of war since it can be produced from raw materials not derived from coal or petroleum. See *Pentaerythritol*.

PETN has the following constants: m.p.,  $141.3^\circ\text{C}.$ ; sp.gr., 1.77; sp.heat (compressed material), 0.4 cal./(gram)( $^\circ\text{C}.$ ); heat of combustion ( $\Delta H_p$ ), 1974 cal./gram. It can be pressed to densities of 1.575, 1.638, 1.71, 1.725, and 1.74 under pressures of 5,000, 10,000, 20,000, 30,000, and 40,000 p.s.i. PETN is insoluble in water, only slightly soluble in ethyl alcohol, ethyl ether, benzene, ethylene dichloride, dichlorobenzene, and cyclohexanol, and somewhat soluble in acetone and methyl acetate.

A boiling 2.5% solution of sodium hydroxide decomposes PETN very slowly, and it is not readily decomposed by a solution of an alkali sulfide. A boiling solution of ferrous chloride decomposes it fairly rapidly. It does not reduce Fehling solution even on boiling. The most practical method for disposal of waste material is to dissolve it in acetone and burn the solution.

Unlike other aliphatic nitrates, PETN is manufactured on a commercial scale by the use of nitric acid rather than a mixture of nitric and sulfuric acids. Practice in the U.S. has consisted of a batch nitration process in which approximately 75 lb. of pentaerythritol is added to 350 lb. of 96% nitric acid in a nitrator, with continuous stirring and cooling of the acid by means of a cold-water jacket. The rate of addition of the pentaerythritol is controlled so that, with an initial acid temperature of  $18^\circ\text{C}.$ , the temperature rises to and is maintained at  $22$ – $23^\circ\text{C}.$  After completion of the addition of pentaerythritol, the stirring and cooling are continued for 20 minutes. The solution is then

run into about 100 gal. of water under agitation in a drowning tank, thus causing the PETN to be precipitated. After being caught on a glass-cloth filter, the precipitated solid is washed with cold water and then suspended in cold water containing a little sodium carbonate. The slurry is then filtered and the solid rewashed with water. The PETN is then dissolved in acetone at 50°C., which contains a little ammonium bicarbonate to neutralize any occluded acidity. After the solution is filtered, the tetranitrate is reprecipitated by the addition of cold water. The precipitated solid is caught in a filter and washed with water to remove the acetone. The water-wet tetranitrate is considered the final product, as the material generally is not dried before being used. The yield of PETN is approximately 93% of the theoretical. The spent acid obtained from the drowning operation contains approximately 20% nitric acid, which is recovered and concentrated for re-use.

The Germans used a basically similar process, which had been made semicontinuous. This was accomplished by having two nitrators connected in series, with the overflow from the first discharging into the second. The overflow from the second nitrator discharged into a pot to which cold water was added continuously. After being caught on a filter and washed almost free from acid, the PETN was purified as described above but in such a manner that the purification as well as the nitration was semicontinuous.

During the period between World Wars I and II, the development of formaldehyde and acetaldehyde as cheap commercial raw materials changed PETN from an expensive, small-production material to one capable of production on a large scale at a not-prohibitive cost. This led to its use on a large scale in ammunition.

The quality of PETN produced is controlled chiefly by that of the pentaerythritol used. The pure raw material melts at 260.6°C., but that used for plant-scale nitration has a melting point of 254°C. or greater and contains 2-3% dipentaerythritol and a small amount of tripentaerythritol. The PETN produced for military use is required to have a minimum melting point value of 140°C., a minimum nitrogen content of 17.50%, and a maximum acid or alkali content of 0.005%. It must be free from grit, contain not more than 0.10% acetone-insoluble material, and a 2.3-gram sample must yield not more than 5.0 ml. gas in 20 hours in the 120°C. vacuum stability test. As the explosive can be shipped only when wet and generally is not used in bulk in a dry condition, it is required that it contain 40% water. Because of this, it is packed in containers similar to those prescribed for lead azide and mercury fulminate.

For testing PETN, standard methods are applicable. The nitrometer is used for determining nitrogen content. Acidity or alkalinity may be determined by dissolving a weighed sample in acetone, precipitating with water, filtering, and titrating the filtrate with standardized alkali or acid.

PETN is not ignited by the spit of flame from a black powder fuse, but can be ignited with a flame. It melts and burns quietly in small quantities if not confined. Its explosion temperature test value of 225°C. is slightly higher than that for nitroglycerin (Table IX). It is of the same order of sensitivity to impact as nitroglycerin and is only slightly less sensitive than dextrinated lead azide. Although it crackles when rubbed in a rough porcelain mortar, it is not unduly sensitive to friction, as indicated by pendulum friction test results. PETN is extremely sensitive to initiation by lead azide and other initiating agents. In the sand test, only 0.03 gram of lead azide is required as compared with 0.10 and 0.25 gram for Tetryl and TNT, respectively.

The brisance of PETN is greater than that of nitroglycerin and exceeded only by that of glycol dinitrate and erythritol tetranitrate. This reflects its high rate of detonation of 8300 m./sec. at a density of 1.70. Its power is correspondingly high, as indicated by Trauzl lead block and ballistic pendulum tests, which indicate it to be of the same order as Cyclonite and at least 50% more powerful than TNT (Table X).



The results of vacuum stability tests (Table XI) show PETN to be only slightly more stable than nitrocellulose and much more stable than nitroglycerin, but much less stable than Tetryl or TNT. While it will withstand storage for 18 months at 65°C. without becoming hazardous or unstable, as indicated by acidity and vacuum stability tests, continued storage has marked effects. The presence in the explosive of as little as 0.01% free acid or alkali accelerates deterioration to a marked degree. PETN is the least stable of any of the standard military bursting-charge explosives; for this reason its use probably will decrease in the future unless necessitated by logistics.

PETN is not unduly toxic, as its solid state and insolubility in water render it difficult to inhale or absorb through the skin. However, experiments have shown that small doses cause decreases in blood pressure and larger doses cause dyspnea and convulsions. In production, frequently laundered clothes and baths are prescribed; and, as the material is always wet, dusting is avoided. Precautions against explosion hazards take the form of carefully spaced buildings, drowning tanks, barricades, etc.

**Dipentaerythritol hexanitrate** or **DPEHN** (hexanitrodipentaerythrite, dipenta),  $(\text{CH}_2\text{NO}_3)_3\text{CCH}_2\text{OCH}_2\text{C}(\text{CH}_2\text{NO}_3)_3$ , formula weight 524.28, is a colorless crystalline solid. It has not been used per se, but usually is present in PETN produced on a large scale and, therefore, is of practical interest. The properties of DPEHN were first described in 1932 by Brün.

DPEHN has the following constants: m.p., 73.6°C.; sp.gr., 1.630<sub>16</sub><sup>15</sup>; heat of combustion ( $\Delta H_7$ ), 2394 cal./gram. It is hygroscopic only to the extent of 0.03%. DPEHN is soluble in acetone, but insoluble in water.

DPEHN can be prepared by nitrating dipentaerythritol in the same manner as that used in the preparation of PETN, or by separation from PETN of ordinary grade through fractional crystallization with moist acetone.

As an explosive, DPEHN is distinguished from PETN by being very slightly more sensitive to impact (Table IX) but less sensitive to heat and initiation. The minimum detonating charge of lead azide for DPEHN is 0.18 gram as compared with 0.03 gram for PETN (Table X). The brisance of DPEHN, as judged by the sand test, is about 90% that of PETN. The rate of detonation of DPEHN at density 1.59 is 94% that of PETN at the same density (7860 m./sec.). The explosive power of DPEHN is 76% that of PETN, as indicated by Trauzl lead block test results, and 80% that of PETN on the basis of their heat of explosion values.

The presence of a few per cent of DPEHN in PETN is not objectionable on the basis of their relative sensitivity and brisance values. However, the results of vacuum stability tests given in Table XI show DPEHN to be distinctly less stable than PETN. This difference is such that PETN containing more than 5% of DPEHN does not comply with the standard 120°C. vacuum stability test requirement for military-grade PETN. For this reason the amount of dipentaerythritol in nitration-grade pentaerythritol is kept at a maximum of 2-3%.

In the course of manufacture of pentaerythritol there is produced some dipentaerythritol, a smaller amount of tripentaerythritol and some polypentaerythritol. The tripentaerythritol forms an octanitrate, which melts at 82-84°C.

**Mannitol hexanitrate** or **MHN** (nitromannite),  $\text{NO}_3\text{CH}_2(\text{CHNO}_3)_4\text{CH}_2\text{NO}_3$ , formula weight 452.17, forms colorless, needle-shaped crystals (m.p. 110.7°C. when pure). The compound has been used for loading commercial blasting caps. It was first prepared in 1847 by Domonte and Menard. See *Alcohols, higher polyhydric*.

MHN has a heat of combustion value ( $\Delta H_p$ ) of 1501 cal./gram. It is readily soluble in acetone, ether, and hot ethyl alcohol, only slightly soluble in cold ethyl alcohol, and insoluble in water.

MHN can be prepared by slowly adding mannitol to five times its weight of nitric acid (sp.gr. 1.51), which has been cooled below 0°C. The temperature is not allowed to rise above 0°C. and the acid is stirred during the addition. Sulfuric acid (sp.gr. 1.84) to the extent of five times the weight of mannitol is added slowly with continued cooling and stirring. The precipitated MHN is caught in a filter and washed with water, dilute sodium bicarbonate solution, and finally with water. The crude material is purified by recrystallization from hot ethyl alcohol. The yield is approximately 93% of the theoretical.

Commercially produced MHN has a melting point of 107–109°C. It is kept wet with water until ready for use, and is dried with extreme care.

Although very sensitive to impact, being comparable with lead azide in this respect, and although it has a relatively low explosion temperature test value (Table IX), MHN is not detonated by the spit of flame from a black powder fuse. At 150°C. it decomposes rapidly without detonation, but it deflagrates at slightly higher temperatures. It can be initiated to detonation by the application of heat to its mixture with the feeble initiator Tetracene. MHN is of the same order of brisance and power as nitroglycerin (Table X), which it resembles with respect to oxygen balance and nitrogen content.

The results of vacuum stability tests (Table XI) indicate MHN to be of the same order of stability as nitroglycerin. However, 75°C. international tests show MHN to be distinctly less stable, as it evolves red fumes in a few hours while nitroglycerin does not do so for several days.

This poor stability of MHN might be expected to preclude its use commercially, but it has been found that the addition of a small amount of a stabilizing agent renders it suitable for such use. 75°C. international tests of stabilized MHN gave the following values for loss in weight before and after storage at ordinary temperatures:

Storage, years	Loss in weight, %	
	Stabilized	Unstabilized
0 .....	0.09	3.5
2 .....	0.25	—
5.5.....	0.44	—

After storage for 2 years, the stabilized MHN required 41 days of heating at 75°C. to cause the evolution of red fumes.

**Nitrocellulose** (more correctly called cellulose nitrate) is a fibrous white solid resembling the cotton linters, cotton fibers, or wood-pulp cellulose from which it is prepared. Completely nitrated cellulose would have three  $\text{—ONO}_2$  groups replacing the three  $\text{—OH}$  groups in the cellulose unit (see Vol. 2, p. 879), and nitrocellulose having the corresponding nitrogen content (14.14%) can be prepared. However, commercial and military grades represent only partial degrees of nitration of the anhydroglucose unit of cellulose (see *Cellulose*; *Cellulose derivatives*).

As the various grades of nitrocellulose are used chiefly in manufacturing lacquers, plastic compositions (see *Cellulose derivatives—plastics*), and propellant powders, and only a little is used in the manufacture of gelatin-type dynamites, the material is not sufficiently recognized as being a powerful detonating explosive. Consideration of

nitrocellulose in this section will be from such a viewpoint rather than as a rapidly burning ingredient of propellants (see also "Propellants").

In 1838 Pelouze prepared nitrocellulose by nitrating paper, but did not recognize it as differing from nitrated starch. In 1846 Schönbein, and later in the same year Böttger, described the material as new and described also its explosive characteristics. Schönbein generally is credited with the discovery of nitrocellulose, and his earliest experiments were in connection with its use as both a propellant and a high explosive. Disastrous explosions during storage and in guns led to abandonment of use of uncolloided nitrocellulose for either purpose.

Various types or grades of nitrocellulose are characterized by their nitrogen contents and the following names are used: pyroxylin, 8–12% nitrogen; pyrocellulose,  $12.6 \pm 0.1\%$  nitrogen; guncotton,  $13.3 \pm 0.1\%$  nitrogen. Pyroxylin is soluble in ethyl alcohol to an extent varying with the nitrogen content, but is insoluble in water and ether. Pyrocellulose and guncotton are insoluble in ether or ethyl alcohol, but are colloiddally dispersed by acetone or ethyl acetate. A mixture of ether and ethyl alcohol disperses pyroxylin and pyrocellulose completely and guncotton partially.

The heat of combustion of nitrocellulose varies with the composition, the following values being representative:

Nitrogen content, %.....	12.0	12.6	13.0	13.2	13.3	13.4
Heat of combustion ( $\Delta H_p$ ), cal./g.....	2448	2410	2358	2332.5	2319.5	2307

Nitrocellulose has no melting point, the material undergoing decomposition at various temperatures without melting.

Nitrocellulose can be hydrolyzed or saponified. The rate of hydrolysis is a function of the temperatures; for highly purified pyrocellulose, the available nitric acid liberated per hour at 50 and 97.5°C. is  $1.11 \times 10^{-5}\%$  and  $510 \times 10^{-5}\%$ , respectively. The presence of free acid accelerates hydrolysis at 50°C. markedly ( $3.25 \times 10^{-5}\%$ ), but saponification is even more rapid ( $68.7 \times 10^{-5}\%$ ). The greater the nitrogen content, the lower the degree of hydrolysis. In the 240-hour hydrolysis test the following values are representative:

Nitrogen content, %.....	11.13	12.62	13.44
Hydrolysis, %.....	1.71	1.22	1.03

In the manufacture of nitrocellulose, the degree of nitration is controlled by varying the composition of the mixed acid used for nitration. The higher the degree of nitration desired, the stronger is the mixed acid with respect to increased sulfuric acid content and decreased water content. Representative mixed acids used for the various types of nitrocelluloses are:

Mixed acid	Pyroxylin	Pyrocellulose	Guncotton
Nitric acid, %.....	35	23	25
Sulfuric acid, %.....	45	61	64
Water, %.....	20	16	11

About 50 lb. of mixed acid is used for each pound of cellulose. Nitration is carried out at ordinary temperatures and usually requires about 30 minutes. The cellulose, after being dried to less than 1% moisture, is added rapidly, care being taken to submerge it beneath the surface of the mixed acid immediately. Stirring of the liquid-solid mixture is maintained throughout the nitration period in order to avoid local overheating. The nitrated cellulose is separated from the spent acid and dropped into a drowning tub of cold water.

Four different processes have been used for the nitration of cellulose, these being the pot, Thompson displacement, centrifugal, and mechanical-dipper processes. The last of these is in

general use today, 32-lb. batches of cellulose being nitrated with 1500 lb. of mixed acid (see Vol. 3, p. 363).

The purification of nitrocellulose is a considerably more difficult and tedious operation than that of nitration, requiring large amounts of water and heat. During nitration, small amounts of cellulose sulfate, which is considerably less stable than nitrocellulose, and nitrated oxycellulose are also produced. Owing to the cell-structure characteristic of cellulose, it is difficult to remove entrapped spent acid, which renders nitrocellulose very unstable during storage. It was because of inability to purify nitrocellulose properly that early work with nitrocellulose gave disappointing results. It was not until 1866-1867 that Abel worked out a purification method capable of yielding satisfactorily stable nitrocellulose. This involved an acid-boiling treatment to hydrolyze any cellulose sulfate present, mechanical pulping to free entrapped acid, and treatments with boiling water to hydrolyze any weaker fractions of nitrocellulose present and to remove free acid.

In practice, the nitrocellulose is transferred from the drowning tank to a large wooden tub containing steam coils and a large volume of water. The acidity of this "sour-boil" water is adjusted to approximately 0.4% and boiling is continued for 40-60 hours, with two or three changes of water during this period. This serves to hydrolyze practically all the cellulose sulfate present. The nitrocellulose then is pulped to the desired fineness, with the addition of sodium carbonate to neutralize any free acid liberated by the crushing of the fibers. This is followed by a 4-hour poaching treatment in which the boiling water is kept faintly alkaline by the addition of sodium carbonate. The poaching treatment is followed by three treatments with boiling water (one of 2 hours and two of 1 hour each). Finally, the material is subjected to at least two  $\frac{1}{2}$ -hour washes with cold water. The total treatment time required for the purification of nitrocellulose by the standard process is from 50 to 80 hours.

In time of major emergency the production of nitrocellulose and, from this, propellant powder, is one of the prime necessities for waging war. The original cellulose raw material was cotton linters, which require relatively little purification before nitration. Increased demand in time of war has led to the development of specially purified and fluffed wood-pulp cellulose, which has been found to be as satisfactory as cotton linters. Both cotton linters and wood pulp are in large supply, and, since the demand for propellants is large, the development of a satisfactory, low-cost, large-volume substitute for nitrocellulose seems improbable.

From the values given in Table X, it is apparent that nitrocellulose is one of the most potent explosives in use. In the dry state, the sensitivity to impact varies somewhat with physical condition, but is of the same order as that of PETN and nitroglycerin. Its explosion temperature test value is only slightly greater than that of nitroglycerin. When ignited, it burns at a rate that increases rapidly with increase in temperature; and, if the nitrocellulose is confined, the burning is transformed into detonation unless the rate of burning is controlled so as to prevent the development of undue pressure. As dry nitrocellulose can be ignited by a spark from the discharge of static electricity, it is a very dangerous material to handle in the dry state. In practice, uncolloided nitrocellulose is not handled in bulk in a dry condition, and the material intended for shipment is wet with not less than 20% of water.

Dry compressed nitrocellulose can be initiated to detonation by a mercury fulminate blasting cap. The brisance of guncotton (Table X) is distinctly lower than that of nitroglycerin, MHN, PETN, and even DPEHN, but it is as great as that of TNT. Trauzl lead block test and heat of explosion values indicate guncotton to be approximately 70% as powerful as nitroglycerin.

The stability of nitrocellulose, even when highly purified, is not as acceptable as might be desired. Vacuum stability test values (Table XI) show it to be less stable than PETN, but it is more stable than nitroglycerin at elevated temperatures. It has been found that nitrocellulose is inherently unstable, decomposing in the absence of moisture at a rate determined by the temperature. At 50 and 97.5°C. the rates of

thermal decomposition of highly purified nitrocellulose are  $0.45 \times 10^{-5}\%$  and  $280 \times 10^{-5}\%$  per hour, respectively.

Since stability of nitrocellulose is so largely determined by its purity, extreme effort is made to insure quality control. This is assured by careful control of the quality of the cellulose nitrated, by using a lengthy purification process, and by submitting the product to certain tests. These test requirements are for nitrogen content, solubility in ether-ethyl alcohol, acetone-insoluble material, 65.5°C. potassium iodide test, and 134.5°C. heat test. The nitrogen content is determined by means of a nitrometer. The 65.5°C. potassium iodide test is a trace test for acidity or similar harmful impurities. The 134.5°C. heat test, which employs normal methyl violet paper as an indicator paper, serves to indicate that the cellulose sulfate content has been reduced to a minimum; the nitrocellulose is normally resistant to heat at that temperature. This test value is not a measure of the low-temperature stability of the nitrocellulose and has not been correlated with the results of surveillance tests at lower temperatures. Representative values for properly purified nitrocellulose of the pyrocellulose and guncotton types are given in Table IV.

TABLE IV. Representative Test Values for Purified Nitrocellulose.

Test	Pyrocellulose	Guncotton
Nitrogen content, %.....	12.6	13.3
Soly. in ether-ethyl alcohol, %.....	99.9	8
Acetone-insoluble material, %.....	Trace	Trace
Ash, %.....	0.4	0.4
Acidity, %.....	0.00	0.00
Cellulose sulfate, %.....	0.003	0.001
65.5°C. KI test, minutes.....	45	45
134.5°C. heat test:		
Salmon pink, minutes.....	35	30
Red fumes, minutes.....	45	40
Explosion, minutes.....	300+	300+

Nitrocellulose is not a generally toxic material, but workers are required to change clothes and take baths frequently. As nitrocellulose is always wet during manufacture, purification, and packing, explosion hazards are very small. Every effort is made to avoid the accidental drying of nitrocellulose because of the fire hazard. Equipment, floors, etc., are "hosed down" frequently to avoid such accidental drying.

**Nitrostarch** (starch nitrate) is a granular friable solid, which is almost identical in appearance with the starch (*q.v.*) from which it is made. Like nitrocellulose, it is composed of nitrated anhydroglucose units (see Vol. 2, p. 879). It differs from nitrocellulose with respect to the number and spatial configuration of such units in the molecule. Nitrostarch is used in the U. S. in the manufacture of blasting powders and demolition explosives. It was first prepared in 1833 by Braconnot.

As in the case of nitrocellulose, nitrostarch is produced in different grades having various nitrogen contents. The nitrogen contents generally are from 13.0 to 13.3%.

Insoluble in water, but soluble in acetone, nitrostarch is dispersed by an ether-ethyl alcohol mixture completely or partially, depending upon the nitrogen content of the material. The colloidal film or mass obtained by removing solvent from a solvent dispersion of nitrostarch is not as tough as that of nitrocellulose. This is attributed to

the much smaller number of anhydroglucose units in the starch molecule than in the cellulose molecule.

Chemically, nitrostarch resembles nitrocellulose with respect to hydrolysis, saponification, etc. It is slightly hygroscopic.

The details of the commercial process for producing nitrostarch have not been published. It can be manufactured from tapioca or cornstarch. In the latter case, the starch is purified by removal of fats and pectin by means of dilute alkali and water washes. The dried material is nitrated by addition to a nitric-sulfuric mixed acid. After separation from the mixed acid, the nitrostarch is purified by washing.

Nitrostarch is more difficult to stabilize by purification than is nitrocellulose. When subjected to "sour-boil" and boiling water treatments, nitrostarch does not have as high 65.5°C. potassium iodide and 134.5°C. heat test values as does nitrocellulose subjected to the same procedures. However, the material can be purified sufficiently to have stability satisfactory for use in commercial explosives. The addition of a small percentage of a stabilizer such as diphenylamine or an antacid material such as calcium carbonate sometimes is made to insure stability.

From the viewpoint of explosive characteristics, nitrostarch approximates nitrocellulose. It is slightly less sensitive to impact, but has a slightly lower explosion temperature test value (217°C.) than nitrocellulose.

The chemical similarity of nitrostarch and nitrocellulose is shown by the equality of their heat of combustion values when their nitrogen contents are the same. This is confirmed by the equality of their determined heat of explosion values. From these facts it is concluded that nitrostarch is the equal of nitrocellulose with respect to brisance and power.

**Cyclotrimethylenetrinitramine** or **Cyclonite** (hexahydro-1,3,5-trinitro-s-triazine (C.A.), Hexogen, T4, RDX) (VI), formula weight 222.13, forms colorless orthorhombic crystals. It has found extensive application as a base charge for detonators and as an ingredient of explosives for shell and bombs. It was first prepared in 1899 by Henning, but it was not until 1920 that von Herz discovered its value as an explosive. During World War II, it was used on a large scale by all the major participants.

Cyclonite has the following properties: m.p. (when pure), 204.1°C.; sp.gr., 1.816 (can be pressed to a density of 1.73 by the application of a pressure of 30,000 p.s.i.); hardness (Mohs' scale), 2-3; sp.heat at 20°C., 0.30 cal./(gram)(°C.); heat of combustion ( $\Delta H_p$ ), 2307.2 cal./gram. Cyclonite is insoluble in water and very slightly soluble in ethyl alcohol, ether, benzene, toluene, chloroform, carbon tetrachloride, and carbon disulfide. It is soluble in other solvents to the extents given in Table V. It is readily soluble also in hot aniline or phenol. Cyclonite dissolves readily in warm concentrated nitric acid. In cold concentrated sulfuric acid, Cyclonite dissolves very slowly, and the solution decomposes on standing.

Boiling dilute sulfuric acid or sodium hydroxide solution hydrolyzes Cyclonite. Twenty parts by weight of a 5% solution of sodium hydroxide can be used to decom-

TABLE V. Solubility of Cyclonite in Various Solvents.

Solvent	Solv., in g./100 g. solvent, at:			
	20°C.	25°C.	50°C.	97°C.
Acetone.....	7.4	—	12.8	—
Cyclohexanone.....	—	12.7	—	25
Nitrobenzene.....	—	1.5	—	12.4
Mesityl oxide.....	—	3	—	12
Methyl acetate.....	2.95	—	6.0	—

pose waste Cyclonite. Upon reduction, Cyclonite yields methylamine, nitrous acid, and hydrocyanic acid, or methylamine, ammonia, nitrous acid, and formaldehyde, depending upon the experimental conditions.

Cyclonite is prepared by nitrating hexamethylenetetramine with concentrated nitric acid. It can be obtained in 68% yield by slowly adding 1 part by weight of hexamethylenetetramine to 11 parts of 100% nitric acid, while the temperature is maintained at 30°C. or less. After being cooled to 0°C., the mixture is stirred for 20 minutes more and then drowned in ice water. The crude material is freed from acid by washing with water and is then recrystallized from acetone or other solvent.

As Cyclonite is obtained from the raw materials formaldehyde, ammonia, and nitric acid, it offers distinct logistic advantages over explosives dependent upon petroleum or coke by-products as basic materials. Like PETN, Cyclonite can be produced if only coal, water, air, and electrical energy are available as starting materials. For this reason, the Germans and Italians emphasized the production and use of this explosive under the names Hexogen and T4.

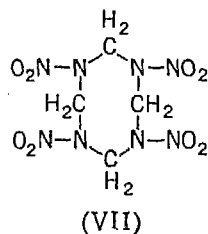
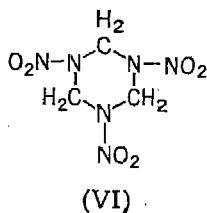
Military grades of Cyclonite are those consisting of essentially pure cyclotrimethylenetrinitramine, as indicated by a melting point of 200°C. or greater, and one containing not more than 12% of cyclotetramethylenetetranitramine (HMX), as indicated by a melting point of not less than 190°C. Either type is required to contain not more than 0.05% acetone-insoluble material and 0.03% inorganic insoluble material. Acidity in the first grade must not exceed 0.05% and in the second grade, 0.02%.

The sensitivity to impact of Cyclonite approximates that of Tetryl (Table IX), but it is somewhat more sensitive to friction and rifle bullet impact. It is also more sensitive to initiation by lead azide or DDNP, but equally sensitive to initiation by mercury fulminate. Increase in temperature increases the sensitivity of Cyclonite to impact; at 105°C. its impact test value is only 5 in.

Cyclonite is of the same order of brisance as PETN, as indicated by sand test and rate of detonation values (Table X). Trauzl lead block and ballistic pendulum test values indicate Cyclonite to be equal to or slightly superior to PETN with respect to explosive power, and their heat of explosion and gas volume values substantiate this comparison. Cyclonite, therefore, may be considered at least the equal if not the superior of any other solid bursting-charge explosive available on a production basis.

The stability of Cyclonite is considerably better than that of PETN (Table XI) and almost as good as that of TNT, as indicated by vacuum stability test values. It withstands storage at 85°C. for 10 months or at 100°C. for 100 hours without measurable deterioration. From the viewpoint of stability, Cyclonite must be considered highly satisfactory.

Cyclonite does not appear to be markedly toxic. No precise data in this connection are available. Daily changes of clothes and baths are prescribed for those working continuously with large quantities of the explosive.



**Cyclotetramethylenetetranitramine** or **HMX** (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (*C.A.*), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (*R.I.*)) (VII), formula weight 296.17, is a white crystalline material, which exists in at least four polymorphic forms. It is formed under some conditions when Cyclonite is prepared by the nitration of hexamethylenetetramine, and, therefore, is of some practical importance although the compound itself has not been used as an explosive.

The most important characteristics of the four forms of HMX are as follows:

Characteristic	$\alpha$ -form	$\beta$ -form	$\gamma$ -form	$\delta$ -form
Specific gravity.....	1.96	1.87	1.82	1.77
Stability (room temp.).....	Metastable	Stable	Metastable	Unstable
Relative insensitivity to impact.....	60	325	45	75

Ordinarily the least-sensitive  $\beta$ -form is produced, and this form will be the one discussed.

HMX has the following properties: m.p., 276–277°C.; hardness (Mohs' scale), about 2; heat of combustion ( $\Delta H_p$ ), 2230.7 cal./gram. It is practically insoluble in water and is nonhygroscopic. Its solubility in other solvents is comparable with that of Cyclonite. In its chemical reactivity it is also comparable with Cyclonite except that it is not easily decomposed by alkaline hydroxide. It is prepared by the nitration of hexamethylenetetramine, the nitrating conditions differing from those used to prepare Cyclonite; a mixture of the two explosives results. The HMX is separated by fractional crystallization or by decomposing the Cyclonite with sodium hydroxide solution. It can also be obtained by the nitrolysis of dinitropentamethylenetetramine.

HMX is of the same order of sensitivity to impact and friction as Cyclonite (Table IX), but is less sensitive to initiation since it has a minimum detonating charge value of 0.17 gram of lead azide as compared with 0.05 gram for Cyclonite. As judged by sand test values, HMX is 92% as brisant as Cyclonite. Ballistic pendulum test values indicate HMX and Cyclonite to be of equal explosive power (Table X).

HMX is even more stable than Cyclonite as judged by vacuum stability test values (Table XI) and explosion temperature test values (Table IX). The results of vacuum stability tests at 150°C. indicate HMX to be of the same order of thermal stability as TNT and ammonium picrate.

The presence of HMX in Cyclonite, therefore, cannot be considered to impair significantly the brisance or stability of the latter; and, if conditions of crystallization are such that the  $\beta$ -form of HMX is produced, its presence does not have an undesirable effect with respect to sensitivity to impact or friction. However, HMX does not offer any sufficiently marked advantage over Cyclonite to warrant its production and use as a substitute for Cyclonite.

**m-Dinitrobenzene** (1,3-dinitrobenzene),  $C_6H_4(NO_2)_2$ , formula weight 168.11, in the pure form consists of almost colorless crystals (m.p. 89.57°C.). The material produced on a commercial basis (m.p. 80–81°C.) has generally consisted of a mixture of isomers containing 91–94% of the meta compound. The material has been used as a substitute for TNT and other high explosives in shell, generally in mixtures with ammonium nitrate or other high explosives. It has also served as a raw material for the manufacture of tetranitroaniline. See *Nitrobenzenes*.



Pure *m*-dinitrobenzene has the following properties:  $b_{770}$ , 302°C.; sp.gr., 1.571<sub>4</sub>; heat of combustion ( $\Delta H_p$ ), 4145 cal./gram. *m*-Dinitrobenzene is soluble in water to the extent of only 0.05 and 0.32 gram/100 grams water at 15 and 100°C., slightly soluble in alcohol, more so in ether, and fairly soluble in benzene, toluene, chloroform, and ethyl acetate. Dinitrobenzene is readily prepared by slowly adding 1 part by weight of nitrobenzene to a mixture of 2.5 parts of sulfuric acid (sp.gr. 1.84) and 1.5 parts of nitric acid (sp.gr. 1.52), which is maintained at about 100°C. After partial cooling, the resulting mixture is poured into cold water, and the precipitated dinitrobenzene is caught on a filter. It is washed a number of times with warm or hot water, allowed to crystallize, and dried.

As an explosive, dinitrobenzene has interesting, if not outstanding, characteristics in view of the ease of its production from a very cheap and readily available raw material—benzene. It is of the same order of brisance as 80/20 Amatol, as indicated by sand test values, and about 87% as powerful as TNT, as judged by Trauzl lead block test and heat of explosion values (Table X). While few data are available, the compound should be less sensitive than TNT or trinitrobenzene. Its rate of detonation at a density of 1.403 has been found to be 6150 m./sec., as compared with 6185 for pressed TNT at the same density.

In spite of these fairly favorable characteristics, dinitrobenzene has been used only to a limited extent because of its extreme toxicity. When forced to use it during World War I because of shortages of more satisfactory explosives, the Germans found it necessary to resort to carton-loading in order to minimize the poisoning of workers. It has an irritating effect on the respiratory system and causes the skin of the victim of its action to become bluish in color. It is considered unsuitable for handling on a mass-production basis and should be handled with care even on a laboratory scale. Contact of the skin with its solution in alcohol or benzene is particularly to be avoided.

**1,3,5-Trinitrobenzene** (*sym*-trinitrobenzene, TNB),  $C_6H_3(NO_2)_3$ , formula weight 213.11, forms rhombic plates of slight yellowish color when crystallized from benzene. This compound is the most powerful of the trinitrated aromatic hydrocarbons, but, because of the low yield obtainable when benzene is nitrated and because of its relatively high melting point, it has had only limited application as an explosive. It nevertheless is of some interest for use in explosive compositions. The compound was first prepared in 1876 by Hepp.

Pure 1,3,5-trinitrobenzene has the following properties: m.p., 123.25°C.; sp.gr., 1.688; vapor pressure, 2 mm. Hg at 175°C., 50 at 250°C.; nonvolatile at room temperature; heat of combustion, 3113 cal./gram. When pressed at 75,000 p.s.i., it has an apparent density of 1.67. The cast material has a density of 1.60–1.61. It is almost insoluble in water (0.0278 and 0.102 gram/100 grams water at 15 and 100°C., respectively). It is soluble in other solvents to the extents given in Table VI. Trinitrobenzene is hygroscopic to the extent of only 0.04%.

When treated with an alkoxide or alcoholic sodium hydroxide, trinitrobenzene forms a sensitive metallic derivative. Continued treatment with alkali results in the formation of 3,3',5,5'-tetranitroazoxybenzene or the replacement of one nitro group to yield 3,5-dinitrophenol. When treated with hydroxylamine in cold alcoholic solution, trinitrobenzene yields picramide (2,4,6-trinitroaniline).

Trinitrobenzene can be prepared by the nitration of *m*-dinitrobenzene, the reduction of trinitrochlorobenzene (picryl chloride), or the oxidation of trinitrotoluene (TNT) to trinitrobenzoic acid, and decarboxylation of this to trinitrobenzene. The yield of trinitrobenzene obtainable by the

nitration of benzene is so low and the amount of nitric acid is so great that this method is too costly, as is the reduction of trinitrochlorobenzene. The most economical method developed to date is the oxidation of TNT by means of sulfuric acid and sodium dichromate. The trinitrobenzoic acid formed is dissolved in water and boiled, with the liberation of carbon dioxide and the precipitation of trinitrobenzene.

The explosive characteristics of trinitrobenzene are comparable with those of TNT and picric acid rather than those of Cyclonite and PETN. It is more sensitive

TABLE VI. Solubility of 1,3,5-Trinitrobenzene in Various Solvents.

Solvent	Soly., in g./100 g. solvent, at:		
	17°C.	32.5°C.	50°C.
Acetone.....	59.11	—	160.67
Ethyl acetate.....	29.83	—	52.40
Toluene.....	11.82	—	76.31
Benzene.....	6.18	—	25.76
Chloroform.....	6.24	—	18.42
Methanol.....	3.76	—	7.62
Ethyl alcohol.....	2.09	—	4.57
Ethyl alcohol, 95%.....	1.39	—	3.52
Ether.....	1.70	2.72	—
Carbon disulfide.....	0.24	—	0.69

to impact than TNT or picric acid, but of the same order of insensitivity to friction and initiation (Table IX). The brisance and power of trinitrobenzene, as would be expected from its constitution, are slightly greater than those of TNT and picric acid, as judged by sand test and Trauzl lead block test values (Table X). These points of superiority are ascribable to the higher rate of detonation and heat of explosion values of trinitrobenzene. Ballistic pendulum test values indicate trinitrobenzene to be 10% more powerful than TNT but of essentially the same power as picric acid.

Trinitrobenzene is one of the most stable, if not the most stable, of known explosives. Its explosion temperature test value of 550°C. is greater than even that of TNT (Table IX), and vacuum stability test values (Table XI) show it to be of at least the same order of stability as TNT and ammonium picrate.

There are no standard grades of trinitrobenzene, and no specification requirements have been established for the material. In view of modern trends in military explosives and the disadvantage of trinitrobenzene in not being readily castable at low-pressure steam temperatures, it is not probable that the future will see any marked development of the use of this explosive.

Although trinitrobenzene has been reported to be toxic, supporting data are not available. It should, therefore, be handled with some care and inhalation in dust form should be avoided.

$\alpha$ - or **2,4,6-Trinitrotoluene** or **TNT** (Trotyl, Triton, Tritol, Tolite, Trilite) (VIII), formula weight 227.13, the most important of modern high explosives, exists in two polymorphic forms; the  $\alpha$ -form is stable at ordinary temperatures. It forms colorless or light yellow rhombohedral crystals, sp.gr. 1.654. TNT has found wide application as a bursting-charge explosive for shell, bombs, and grenades, as an ingredient of binary explosives such as the Amatols, and as an ingredient of propellant com-

positions. It was first prepared in 1863 by Wilbrand, but it was not until 1891 that it was prepared on an industrial scale, in Germany. By 1901 its use began to displace that of picric acid and it was adopted by all the military powers. World War I saw its use expanded to the maximum permitted by the available supply of toluene, and World War II saw TNT become even more important and extensively applied. See *Toluene*.

Pure TNT has a freezing point of  $80.75 \pm 0.05^\circ\text{C}.$ ; this characteristic is determined more reproducibly than the melting point. Its vapor pressure values are:

Temperature, $^\circ\text{C}.$ .....	85	100	190	245-250
Vapor pressure, mm. Hg.....	0.053	0.106	2	50

At ordinary temperatures TNT is essentially nonvolatile. It may be distilled in a vacuum without decomposition.

Specific heat values are:

Temperature, $^\circ\text{C}.$ .....	0	20	50	80
Sp.heat, cal./(gram)( $^\circ\text{C}.$ ).....	0.309	0.328	0.353	0.374

Other thermal properties of TNT are: heat of fusion, 21.41 cal./gram; heat of combustion ( $\Delta H_p$ ), 3589.5 cal./gram; thermal conductivity at  $25^\circ\text{C}.$ , 0.00055 cal./ (sec.)(sq.cm.)( $^\circ\text{C}./\text{cm}.$ ). The coefficient of linear expansion of cast TNT varies somewhat with crystal size, but for medium-size crystals it is  $7.7 \times 10^{-6}$  in./in./ $^\circ\text{C}.$  over the range  $-40$  to  $60^\circ\text{C}.$

Crystals of TNT have index of refraction values of  $\alpha = 1.5430$ ,  $\beta = 1.6742$ , and  $\gamma = 1.717$  for sodium light. They have a hardness of 1.2 on the Mohs scale. When pressed to a density of 1.6, TNT has a compressive strength of 1400 p.s.i. and a modulus of elasticity of  $5.4 \times 10^{10}$  dynes/sq.cm.

On melting, TNT undergoes an expansion in volume of approximately 12%, and the density of the liquid is 1.465. Freezing of the liquid causes a corresponding contraction in volume, and this characteristic is the basis for certain difficulties in the melt-loading of the explosive. Because of the practical importance of molten TNT, extensive study has been made of its characteristics. It has a viscosity of 9.5 centipoises at  $100^\circ\text{C}.$  The explosive characteristics of liquid TNT will be considered later.

Cast TNT has a density of 1.55-1.56, but the crystalline material can be pressed to a density of 1.6 when subjected to a pressure of 50,000 p.s.i.

TNT is almost insoluble in water (0.010, 0.013, and 0.1475 gram/100 grams water at 0, 20, and  $100^\circ\text{C}.$ , respectively) and is hygroscopic to the extent of only 0.03%. It is soluble in other solvents at  $20^\circ\text{C}.$  to the extents given in Table VII.

**TABLE VII. Solubility of TNT in Various Solvents at  $20^\circ\text{C}.$**

Solvent	Soly., g./100 g. solvent	Solvent	Soly., g./100 g. solvent
Ethyl ether.....	3.29	Chlorobenzene.....	33.9
Ethyl alcohol, 95%.....	1.23	Carbon disulfide.....	0.48
Acetone.....	109	Methyl acetate.....	72.1
Carbon tetrachloride.....	0.65	Sulfuric acid.....	4
Chloroform.....	19	Benzene.....	67
Ethylene dichloride.....	18.7	Toluene.....	55
Trichloroethylene.....	3.04		

As compared with Tetryl and picric acid, TNT is relatively, but not entirely, nonreactive. Alkalies, alkoxides, and ammonia react with it to form dangerously sensitive compounds. A mixture of TNT and solid potassium hydroxide bursts into flame when heated to only 80°C. Sodium sulfide decomposes it completely with the formation of nonexplosive products, and this reaction can be used for the disposal of waste material. Sodium sulfite also decomposes TNT, with the formation of a red, water-soluble product. TNT reacts with formaldehyde to yield 2,4,6-trinitrophenyl-ethanol (2,4,6-trinitrophenethyl alcohol), and with benzaldehyde to form 2,4,6-trinitrostilbene. It forms molecular complexes with amines such as aniline, toluidine, naphthylamine, and carbazole. Upon oxidation with chromic or nitric acid, TNT is converted into 2,4,6-trinitrobenzoic acid. Exposure to sunlight or ultraviolet light, particularly in the presence of oxygen, results in decomposition and discoloration with consequent reduction in the freezing point and increase in sensitivity to impact.

TNT can be prepared from toluene by one-, two-, or three-stage nitration processes, and all three processes have been used industrially (see *Nitration*). However, it has been found that the three-stage process offers the advantages of maximum yield, greater purity of product, and greater ease of control of acid concentration and temperatures involved. The three-stage process was in general use during World War II, and a general description of this process is as follows:

Approximately 12,500 lb. of "mono-mix" acid is transferred to the nitrator in the "mono-house" and cooled, with agitation, to 36–38°C. The mono-mix acid is prepared by "butting-up" with weak nitric acid the "bi-spent" acid from the second nitration stage, and it contains approximately 48% sulfuric acid, 14% nitric acid, 17% nitrosylsulfuric acid, 19% water, and 2% nitro compounds. Then 1600 lb. of toluene is added under the surface of the acid at such a rate that the temperature increases 1°C. per minute. The temperature at the completion of nitration is about 55°C., and this is allowed to increase to 57°C. The stirring is reduced and the charge cooled to 38°C. Stirring is then discontinued, and the spent acid is allowed to separate and settle. The "mono-waste" acid is drawn off and transferred to the recovery system for reworking. The "mono-oil" is transferred to the scale tank of another building some distance away for second-stage nitration.

Spent acid from the trinitration is transferred to the nitrator in the "bi-house" and cooled, with stirring, from 88 to 77°C. Weak nitric acid is added so that the nitrator finally contains about 12,500 lb. acid composed of 54% sulfuric acid, 13% nitric acid, 17% nitrosylsulfuric acid, 8% water, and 8% nitro compounds. With continued stirring the mono-oil is added at such a rate that the temperature of the mixture rises to 82°C. and then more slowly to 85°C. The charge is "cooked" at this temperature for 8 minutes and then cooled to 77°C. After the "bi-oil" has separated, the lower layer of bi-spent acid is drained off and transferred to a fortifier for butting-up to form mono-mix. The bi-oil is drained into a storage tank before transfer to the "tri-house" for trinitration.

A "tri-mix" acid is prepared in a scale tank by adding to oleum a "semi-mix" acid containing 62% total (equivalent) sulfuric acid and 43% nitric acid. The tri-mix contains 82.7% total sulfuric acid and 23.3% nitric acid, and generally is at a temperature of about 85°C. Approximately 8500 lb. of the tri-mix is transferred to the nitrator in the tri-house, agitated, and cooled to 80°C. The bi-oil is now added at such a rate that the temperature of the mixture increases about 0.5°C. per minute to a maximum of 90°C. After the completed charge has been held at that temperature for a few minutes, it is allowed to rise to 110°C. at the rate of 1°C. per minute. The temperature is maintained at 110°C. for about 20 minutes and then cooled to 107°C. with continued agitation. Stirring then is discontinued, and the "tri-oil" is allowed to separate and form a top layer, while the temperature decreases to about 93°C. The bottom layer of "tri-spent" is drained off to the binitrator, and the tri-oil (approximately 3500 lb.) is then drained off and pumped to the washhouse for purification.

The quality of the crude TNT may vary widely with the degree of control and efficiency of the third stage of nitration. If this is not complete, a significant amount of dinitrotoluene will be present. The chief impurities normally present are  $\beta$ - or 2,3,4-trinitrotoluene (m.p. 112°C.) and  $\gamma$ - or 3,4,6-trinitrotoluene (m.p. 104°C.). Trinitrobenzoic acid, trinitrobenzene, and tetranitromethane in smaller amounts are also present, due to the oxidizing action of nitric acid. When free from acid, such crude TNT contains 5–7% impurities and has a freezing point of only 75–76°C. The purifica-

tion of the material is an important step in production, since the oily crude TNT is relatively insensitive to initiation and is subject to exudation when stored at only slightly elevated temperatures.

Before World War I, purification was accomplished by washing the crude to remove nitric acid and most of the tetranitromethane and recrystallizing from ethyl alcohol, carbon tetrachloride, or sulfuric acid. Another method was to wash the TNT free of acid while in the molten condition, crystallize, and then wash with hot acids, which dissolved the impurities on the surfaces of the crystals. During World War I, the Sellite (sodium sulfite) process of purification was introduced, and this became standard during World War II. This process permits the rapid and very effective purification of crude TNT.

In the Sellite process, the tri-oil is agitated for a few minutes with a small amount of hot water to dissolve any free acid present. Sufficient cold water is added to cool the mixture to 68°C. and cause the crystallization of the TNT. Sufficient alkali is added to neutralize any free acid in solution, but care is taken to avoid an excess, since this would decompose some TNT. To the agitated suspension of crystalline TNT in water is now added, first slowly and then more rapidly, a calculated quantity of a solution containing 16–17% sodium sulfite and 0.1–0.3% sodium hydrogen sulfite. Usually this requires 15 minutes, and the color of the liquid becomes deep red. Agitation is continued for about 15 minutes, and the mixture is then transferred to wringers where the TNT is held and the "red water" is separated and transferred to catch boxes for disposal. The TNT is washed with water to remove any adhering red water and is then transferred to a "melt tank," where it is melted and washed well with hot water and then dried by agitation with dry air at 100°C. or more. The molten TNT is then cooled and flaked or grained.

Sodium sulfite does not react with dinitrotoluene, so the nitration process must be controlled so as to insure practically complete nitration to the trinitro condition. It reacts with the  $\beta$ -TNT and  $\gamma$ -TNT, present on the surfaces of the  $\alpha$ -TNT crystals, to form the sodium salts of the corresponding dinitrotoluenesulfonic acids. These salts are easily soluble in water and so are removed. The hot sodium sulfite reacts with a little of the  $\alpha$ -TNT to form hexanitrobibenzyl, which is responsible for the color of the red water. Another purification reaction is that of sodium sulfite and tetranitromethane to form sodium trinitromethanesulfonate and sodium nitrite, both of which are readily soluble in water. Any small amount of dinitrotoluene present generally is removed by the mechanical action of washing. The sodium hydrogen sulfite takes no part in the purification reactions, but is added for its buffer action in maintaining neutrality.

The TNT obtained by the Sellite purification process generally has a freezing point of  $80.3 \pm 0.1^\circ\text{C}$ ., but, by increasing the duration of the Sellite treatment, a product having a freezing point as great as  $80.6^\circ\text{C}$ . can be obtained.

Until 1940, the capacity of any country to produce TNT was limited by the availability of toluene as a by-product of the coke industry. The development of special hydrogenation and polymerization processes has since made it available from petroleum fractions and by-products. As a result, a country such as the U.S., which has both coal and petroleum resources, has a greatly enhanced TNT production potential; and, during World War II, this country had available any required amount of toluene. During World War I, TNT was a critical material in all countries, and its dilution with weaker explosives was necessary in order to extend its use as far as possible. During World War II, Germany suffered from a shortage of TNT, having limited petroleum resources; however, the U.S. had available so much TNT that it became the suspension agent for more powerful explosives, such as PETN and Cyclonite, that could thus be applied in ammunition by melt-loading methods.

Grades of TNT vary from country to country, these being determined chiefly by purity, as reflected by the freezing point. In the U.S., Grade I TNT is required to have a minimum freezing point of  $80.2^\circ\text{C}$ ., while in Canada this is only  $80.0^\circ\text{C}$ . Other requirements limit the free acidity to 0.01%, alkalinity to nil, and insoluble matter to 0.05%. In order to insure efficient final washing of the purified TNT, the sodium content is not permitted to exceed 0.001%. This is determined by ashing a sample, dissolving the ash, and precipitating sodium as sodium magnesium uranyl acetate.

TNT is, with the exception of ammonium picrate, the least sensitive to impact of the standard military explosives (Table IX). It explodes only occasionally in the rifle bullet test, is quite insensitive to friction, and has next to the highest explosion temperature test value. Although less sensitive to initiation than Tetryl, it is of the same order of sensitivity as trinitrobenzene and picric acid.

Sublimed TNT is deposited occasionally during plant operations in cold weather. This if of high purity and in a state of very fine subdivision; and it has been found to be only slightly less sensitive to impact than Tetryl but nearly as insensitive to initiation as ordinary TNT.

Foreign materials, particularly those of a gritty nature, make TNT much more sensitive to impact. A mixture of equal parts of TNT and rust is as sensitive to impact as Tetryl, although not noticeably more sensitive to friction than TNT itself.

Molten TNT is a dangerously sensitive material when properly confined, as shown by the impact test values given in Table VIII. The lowest values indicate confined molten TNT to be of the same order of sensitivity as mercury fulminate. Because of this, special care must be observed in the handling of large quantities of molten TNT, as in melt-loading operations.

TABLE VIII. Impact Test Values of Molten TNT.

Temperature, °C.	State	Impact test, in.
-40 .....	Solid .....	17
20 .....	Solid .....	14
80 .....	Liquid.....	7
90 .....	Liquid.....	3
105-110.....	Liquid.....	2

With the exception of ammonium picrate and initiating agents, TNT is the least brisant of the standard military high explosives. However, its brisance, as judged by sand test values, is 81% that of Tetryl and 91% that of picric acid (Table X); and the rate of detonation of TNT at a density of 1.6 is 93% that of Tetryl and 99% that of picric acid at the same density. As measured by their Trauzl lead block test, ballistic pendulum test, and heat of explosion values, TNT is approximately 78% as powerful as Tetryl. From this, it is not to be inferred that TNT is an undesirably weak explosive. It has been found capable of giving very acceptable fragmentation and blast effects when loaded in grenades, shell, and bombs.

TNT is one of the most stable, if not the most stable, of bursting-charge explosives. Vacuum stability tests (Table XI) show it to undergo relatively little, if any, decomposition in 40 hours at 150°C. It has been stated that decomposition does not begin until a temperature of 180°C. is reached. TNT has been found to be unchanged after storage for 20 years at ordinary temperatures. It has been stored at 65°C. for 1 year and at 75°C. for 6 months without undergoing any deterioration. Molten TNT has been kept at 85°C. for 4 weeks without any evidence of decomposition. Samples of TNT have been solidified and remelted fifty times without deterioration as indicated by freezing point, acidity, vacuum stability, and impact tests. The chemical stability of TNT represents no practical problem; but, storage at elevated temperatures may cause physical instability, as reflected by the exudation of an eutectic mixture of impurities and  $\alpha$ -TNT as an oil. TNT that has a freezing point of 80.2°C. withstands storage at 50°C., but exudes at 65°C. when loaded in shell. Under

such conditions a freezing point greater than 80.4°C. is required to prevent exudation at 65°C. TNT that has a freezing point of 80.75°C. undergoes no exudation at 70°C. While continued exposure to light causes some deterioration and discoloration, this is a surface effect and is of no practical importance, since TNT rarely is subjected to such exposure in very thin layers.

TNT is somewhat toxic, but not extremely so, and has no vesicant or lacrimatory action. A maximum concentration in air of 1.5 mg. per cubic meter has been suggested to avoid undue toxicity. Daily changes of clothes and baths are required of those working with TNT in quantity. It is classified as not dangerous with respect to hazard from sparks resulting from static charges of electricity.

**Picric acid** (*q.v.*) (2,4,6-trinitrophenol, Melinite, Lyddite, Pertite, Shimose) (IX), formula weight 229.11, exists in two polymorphic forms. When crystallized from alcohol it takes the form of yellow, orthorhombic, flattened rods. First prepared in 1771 by Woulff, it was used as a yellow dye for silk and wool; and it was not until after 1885 that the French began to use it as a bursting charge for shell under the name of Melinite. In 1888, Great Britain began to use it under the name of Lyddite. It, therefore, was the first modern high explosive used for this purpose. Picric acid, alone or in admixture with other materials, was the chief high explosive of all the military powers until displaced by the development of TNT. It has been used as the explosive in detonating fuse and an ingredient of pyrotechnic compositions as well as a bursting-charge explosive.

Picric acid is of very low volatility at ordinary temperatures, but because of its bitter taste and dustiness it has the effects of a more volatile material; m.p., 122.5°C.; dec. above 300°C.; sp.gr., 1.763; vapor pressure, 2 mm. Hg at 195°C., 50 at 255°C.; heat of fusion, 20.4 cal./gram; heat of combustion ( $\Delta H_p$ ), 2671.5 cal./gram; sp.heat, 0.234 cal./(gram)(°C.) at 0°C., 0.274 at 50°C., 0.318 at 100°C. The density of cast picric acid is approximately 1.64, but it can be compressed to a density of 1.725 when subjected to a pressure of 100,000 p.s.i.

Although soluble in water to the extent of 1.4 and 6.8 grams/100 grams water at 20 and 100°C., respectively, picric acid is almost nonhygroscopic (0.05%). Its solubility in ether is only 1.43 grams/100 ml. ether and in ethyl alcohol 4.9 grams/100 ml. alcohol at 20°C. The compound is easily soluble in benzene, nitric acid, and sulfuric acid.

Picric acid is chemically active. It decomposes carbonates, and may be titrated with bases by the use of sodium alizarinsulfonate as an indicator. When a copper ammonium sulfate solution is added to an aqueous solution containing as little as 0.01% of picric acid, a green precipitate is produced. Neutral lead acetate produces no precipitate, but, if the acetate is basic or ammoniacal, a bright yellow precipitate of lead picrate is obtained. Picric acid also yields precipitates of picrates of acridine, cinchonine, and nitron. It reacts with all the common metals to form picrates, some of which are extremely sensitive.

As the direct nitration of phenol is so vigorous that it can be controlled only with great difficulty, the manufacture of picric acid is carried out by first treating phenol with sulfuric acid to form a mixture of phenolsulfonic acids and then nitrating. Various processes have been described, varying from one-stage to three-stage nitration. The best yield claimed is 200 parts of acid per 100 parts of phenol. Another process is the conversion of dinitrochlorobenzene into dinitrophenol by means of sodium hydroxide and nitration of the dinitro compound. The catalytic process for producing picric acid directly from benzene involves the use of mercuric nitrate and concentrated nitric acid.

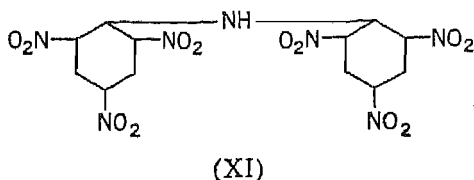
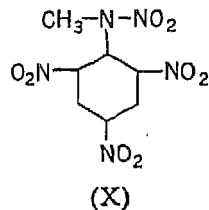
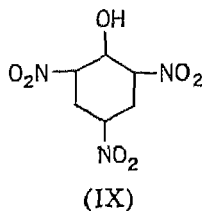
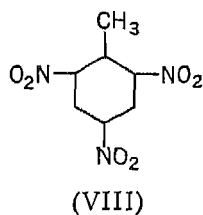
The grade of picric acid standard for military use is required to have a minimum melting point value of 120.0°C. and contain not more than 0.2% ash, 0.2% water-insoluble material, 0.1% sulfuric acid, and 0.0004% lead. It must be free from nitric acid.

Picric acid has been displaced largely by TNT and other explosives, but was used in both World Wars by the Germans because of a shortage of TNT. Its disadvantages are its high melting point, which increases the difficulty of melt-loading the explosive, and its tendency to react with metals. A number of serious accidental explosions of picric acid have been attributed to the presence of metallic picrates.

Picric acid has properties intermediate between those of trinitrobenzene and TNT (Table X). This is true of stability (Table XI) as well as sensitivity (Table IX), brisance, rate of detonation, and explosive power.

Picric acid has a strong staining action on the skin, but is not as toxic as some of the comparable nitro compounds. Nevertheless, its dust should not be inhaled, and frequent baths and changes of clothes are prescribed.

The metallic derivatives of picric acid are well known and, in general, are considered undesirable when formed by the action of picric acid on containers, etc. Potassium picrate has been used in pyrotechnic compositions and detonator compositions. Ammonium picrate is used as a bursting-charge explosive and has been used in propellant compositions. It is much less sensitive than TNT, but lead picrate is extremely sensitive to impact, heat, and friction. The picrates of iron, nickel, zinc, copper, etc., have been considered dangerously sensitive, and their formation has been suggested as the cause of picric acid explosions. Recent work has shown such picrates to be much less sensitive than previously supposed and, in some cases, less sensitive than ammonium picrate. The picrates of iron, chromium, and nickel are of the same order of sensitivity as PETN or Cyclonite when anhydrous, but are much less sensitive than ammonium picrate when hydrated. As they can be formed only in the presence of moisture and dehydrate only at temperatures of 80°C., the formation and presence of the more sensitive forms are unlikely. The picrates of sodium and potassium are much less sensitive than ammonium picrate.



**Ammonium picrate** (ammonium trinitrophenolate, Explosive D),  $(\text{NO}_2)_3\text{C}_6\text{H}_2\text{O}-\text{NH}_4$ , formula weight 232.13, exists in stable yellow and metastable red forms of ortho-



rhombic crystals. The two forms are easily interconvertible, and appear to differ only in color. The material is used as a military explosive for the loading of armor-piercing shell because of its relative insensitivity to impact. It was formerly used in admixture with potassium nitrate as a substitute for black powder. The compound was first prepared in 1841 by Marchand; however, it was not until 1869 that it was used as an explosive by Brugère, who used it in admixture with potassium nitrate.

Ammonium picrate has the following properties: m.p., 265–271°C. (dec.); sp.gr., 1.717 (can be pressed to a density of 1.64 by the application of a pressure of 100,000 p.s.i.); heat of combustion ( $\Delta H_p$ ), 2745 cal./gram. It is soluble in water to the extent of 1.1 and 74.8 grams/100 grams water at 20 and 101°C., respectively, but is only slightly soluble in ethyl alcohol and practically insoluble in ether. It is more soluble in acetone and less soluble in ethyl acetate than in ethyl alcohol. The yellow form is produced by recrystallizing the red form several times from water. The red form is obtained when ammonium picrate is produced in the presence of an excess of ammonia.

Chemically, ammonium picrate is not very reactive. It is decomposed into picric acid and ammonia by strong alkalies. At 0°C. it absorbs one molecule of ammonia, but loses it at 26°C. When maintained at its melting point, it decomposes into the same products. The manufacture of ammonium picrate is relatively simple. Picric acid is suspended in hot water, in which it is only slightly soluble, and neutralized by the addition of gaseous or aqueous ammonia. As the picrate is formed, it goes into solution, and, on cooling the solution, the picrate crystallizes out. If a marked excess of ammonia is used, the red form is obtained. The precipitated picrate is washed with water to remove any excess of ammonia and dried.

The standard grade of ammonium picrate is required to contain not more than 0.025% free acid or alkali, 0.1% water-insoluble material, 0.1% moisture, or 0.1% chloroform-soluble material. It must contain 5.60–5.75% ammoniacal nitrogen, which may be determined by treating the picrate with sodium carbonate solution and distilling the liberated ammonia into an excess of standardized sulfuric acid. It may also be determined by adding 1 gram of the sample, dissolved in 150 ml. water, to 20 ml. 20% formaldehyde solution, which has been exactly neutralized to phenolphthalein with sodium hydroxide. The mixture is heated to 60°C. and titrated with standard alkali solution, using phenolphthalein as the indicator.

As an explosive, ammonium picrate is remarkable chiefly for its insensitivity to shock, which permits its use in armor-piercing projectiles. It is the least sensitive to impact of any of the high explosives used for military purposes (Table IX). Because of its relatively low explosion temperature test value, it is slightly sensitive to frictional impact as indicated by rifle bullet test results. It is also relatively insensitive to initiation, as it cannot be detonated completely by either lead azide or mercury fulminate in the sand test. Complete detonation can be accomplished by using DDNP or Tetryl. When stored at 50°C. for 2 years, ammonium picrate is sensitized so that it can be detonated by mercury fulminate alone. Subsequent storage at ordinary temperature restores its previous insensitivity.

Ammonium picrate is approximately 85% as brisant as TNT, as indicated by sand test values (Table X). Fragmentation tests in shell have indicated it to be about 95% as brisant as TNT. Both explosives have about the same rate of detonation at a density of 1.56, so approximate equality of brisance would be expected. The rate of detonation of ammonium picrate has been found to be somewhat affected, particularly at lower loading densities, by the granulation of the material, but the effect is not pro-

nounced. The power of ammonium picrate is approximately 85% that of TNT, as judged by their heat of explosion values, but the ballistic pendulum test indicates the picrate to be 98% as powerful as TNT.

The stability of ammonium picrate, as judged by vacuum stability test values (Table XI), is greater than even that of TNT and certainly is as great as that of any other high explosive. The material has been found to withstand storage at ordinary temperatures for 20 years with no evidence of deterioration and at 50°C. for over 5 years without marked deterioration.

Ammonium picrate is not markedly toxic, but it discolors the skin and may cause a dermatitis to develop on some individuals. Frequent baths and changes to freshly laundered clothes are prescribed for those working with the material in quantity. Inhalation of the dust should be minimized.

**Tetryl** (2,4,6-trinitrophenylmethylnitramine, *N*-methyl-*N*,2,4,6-tetranitroaniline (C.A.), Tetralite, Pyrenite, CE) (X), formula weight 287.15, is colorless when freshly prepared and highly purified, but rapidly acquires a yellow color when exposed to light. As ordinarily manufactured, it has a light yellow or buff color. When crystallized from benzene, it forms monoclinic prisms. Tetryl has been used chiefly as a booster explosive because of its ease of initiation and high rate of detonation, but it has been used to some extent in the formulation of binary explosives. The compound was first described in 1877 by Martens, but it was not until World War I that it appears to have been used as an explosive. In the early literature, it was frequently designated as tetranitromethylaniline.

Chemically pure Tetryl has a melting point of 129.45°C., but that manufactured for military use may have a melting point as low as 128.75°C. Crystals of Tetryl have a hardness of less than 1 on the Mohs scale. It undergoes slight decomposition when melted, and repeated melting and cooling rapidly increases the degree of decomposition. The cast material has a density of 1.62, but the crystalline material (true sp.gr. 1.73) can be pressed to a density of 1.71 when subjected to a pressure of 30,000 p.s.i.

Specific heat values are:

Temperature, °C.....	0	20	50	100
Sp.heat, cal./(gram)(°C.).....	0.213	0.217	0.223	0.231

Other thermal properties are: heat of fusion, 20.6 cal./gram; heat of combustion, 2914 cal./gram.

Tetryl is very soluble in acetone. Benzene will hold a greater amount in solution if a solution with solid Tetryl present is cooled to a given temperature than if a mixture of solid and benzene is heated to and maintained at that temperature. Representative values for the two equilibriums are:

Temperature, °C.....	15	25	35	45	55
Subsolubility, g./100 g. benzene.....	3.9	5.5	7.4	9.7	13.25
Supersolubility, g./100 g. benzene.....	10.2	12.2	14.9	18.25	22.5

Tetryl is of approximately the same order of solubility in ethylene dichloride:

Temperature, °C.....	0	20	40	60	80
Soly., g./100 g. ethylene dichloride.....	1.5	3.8	7.7	18.8	64.5

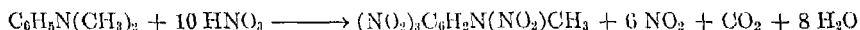
It is almost insoluble in water:

Temperature, °C.....	0	50	100
Soly., g./100 g. water.....	0.005	0.0195	0.184

It is only slightly soluble in ethyl alcohol, ether, carbon tetrachloride, chloroform, or carbon disulfide. The spent acid resulting from the production of Tetryl holds only 0.3% of its weight of Tetryl in solution.

An aqueous alkali reacts with Tetryl to form a metallic picrate and nitrite and methylamine. Prolonged boiling with dilute sulfuric acid has no effect, but, if a solution of Tetryl in cold concentrated sulfuric acid is allowed to stand, 2,4,6-trinitrophenylmethylamine (*N*-methylpicramide) and nitric acid are formed. In the nitrometer, in the presence of mercury, the nitric acid is reduced to nitric oxide, and this can be measured. In benzene solution, at ordinary temperatures, Tetryl reacts with aniline with the formation of 2,4,6-trinitrodiphenylamine (m.p. 179.5°C.) and methylnitramine (*N*-nitromethylamine). When heated under certain conditions, Tetryl yields picric acid with or without the simultaneous formation of *N*-methylpicramide. Tetryl is completely decomposed into nonexplosive, water-soluble products by the action of sodium sulfide, and this reaction can be utilized for the disposal of waste material. The Tetryl is added slowly, with stirring, to an aqueous solution containing 13% by weight of hydrated sodium sulfide. Tetryl is decomposed into nonexplosive products by a 10% by weight solution of sodium sulfite, but the reaction is relatively slow unless the solution is heated to 80–90°C.

The most obvious method for the production of Tetryl—the nitration of *N*-methylaniline—has not been found practical because of difficulty in producing the raw material in a necessary state of purity on a large scale and at low cost. For many years, the standard method of manufacture was the nitration of *N,N*-dimethylaniline:



This process has the disadvantage of requiring nitric acid for the removal of one methyl group by oxidation. It involves the four steps of introducing two nitro groups into the benzene ring, oxidation of one methyl group and its replacement with hydrogen, introduction of the third group into the ring, and, lastly, replacement of the amino hydrogen by a nitro group. In practice, one part of dimethylaniline is dissolved in 14.4 parts of 96–99% sulfuric acid at 20–30°C., dimethylaniline sulfate being formed. The nitration is carried out by the addition at 68–72°C. of 9.2 parts of mixed acid containing 66.7% nitric acid and 15.8% sulfuric acid. Care must be taken that the amount of water present is kept low or benzene-insoluble impurities, which are benzidine derivatives, will be formed. During the nitration, some 2,3,4,6-tetranitrophenylmethylnitramine (*m*-nitrotetryl) (m.p., 146–147°C.) is formed, but this readily undergoes hydrolysis to 2,4,6-trinitro-3-hydroxyphenylmethylnitramine (3-methylamino-2,4,6-trinitrophenol), which is soluble in water and readily removed during the purification of the Tetryl.

With the development of methylamine as a cheap commercial bulk chemical, the production of Tetryl by a method less wasteful of nitric acid became practicable. This involves the reaction of methylamine with 2,4- or 2,6-dinitrochlorobenzene to form dinitrophenylmethylamine (*N*-methyl-dinitroaniline), which is nitrated to Tetryl. This process has seen considerable practical application in recent years.

Because of the formation of some of the tetranitro compound during nitration and the extremely deleterious effect of occluded acidity on the stability of Tetryl, the crude material must be subjected to a careful purification process. This involves removal of most of the acidity by washing with cold water, and treating with boiling water to hydrolyze any tetranitro compound present. Residual acidity is removed by solution in benzene, washing the solution with water, and recrystallization, or by solution in acetone and precipitation of the Tetryl by mixing the solution with water. The benzene or acetone is recovered by distillation for subsequent use. When acetone is used, the purification process can be made continuous.

The only standard grade of Tetryl is that used for military purposes. The essential requirements for this grade are that the material have a minimum melting point value of 128.8°C. and contain not more than 0.02% free acid and 0.10% benzene-in-

soluble material. In order to prevent the presence of any sodium or other metallic derivatives, it is specified that during purification no sodium carbonate or other alkali shall be added to the wash waters used.

As an explosive, Tetryl possesses a combination of characteristics that renders it suitable for use as a booster charge. It is distinctly more sensitive to impact than TNT, somewhat more sensitive to friction and very much more sensitive to the impact of a rifle bullet (Table IX). This degree of physical sensitivity is not such as to require its being packed or stored in a water-wet condition. Tetryl is markedly more sensitive than TNT to initiation by lead azide or mercury fulminate, which is a distinct advantage. The much greater brisance of Tetryl than TNT, as judged by sand test values, reflects its much higher rate of detonation (Table X). It is this greater rate of detonation that renders it so effective as a booster explosive for detonating less-sensitive explosives such as TNT and Amatol. Tetryl is about 128% as powerful as TNT, as indicated by Trauzl lead block and ballistic pendulum tests, but their heat of explosion values would indicate Tetryl to be only 112% as powerful as TNT. Tetryl is only slightly hygroscopic (0.04%), and so its handling and storage involve no problems in this direction.

Although Tetryl is slightly less stable than TNT, as judged by vacuum stability tests (Table XI), and undergoes slight decomposition on melting, which TNT does not, the compound has satisfactory stability. It has been found to withstand storage at ordinary temperatures for 20 years, at 65°C. for 12 months, at 75°C. for 6 months, and at 100°C. for 100 hours without significant deterioration. Because its melting point is so much higher than any practical storage temperature and because of the almost complete absence of impurities that could form eutectic mixtures, the physical deterioration and desensitization of Tetryl by exudation has never been a problem.

Tetryl has a strong coloring action on the human skin and can cause a dermatitis. The use of a cold cream containing 10% sodium perborate has been found to minimize these effects. The use of protective clothing and frequent baths are standard precautions taken to protect the worker in direct contact with quantities of Tetryl. Inhalation of Tetryl dust is recognized as having toxic effects, and the suggested permissible maximum concentration of the dust in air is 1.5 mg. per cubic meter of air.

The future expansion of the uses of Tetryl is rather improbable because of the present availability of even more brisant, stable, and sensitive explosives such as Cyclonite. The use of these newer explosives in the future may actually result in a decrease of the scope of application of Tetryl.

**Hexanitrodiphenylamine** or **Hexite** (Hexil) (XI), formula weight 439.22, in its pure form consists of yellow orthorhombic needles (m.p. 243.5–244.5°C. with decomposition). As ordinarily manufactured it is brownish yellow (m.p. 240–245°C.). It is a powerful vesicant and injurious to the mucous membranes. The compound was first described in 1874 by Austen and studied as an explosive in 1891 by Hausermann. In World Wars I and II, it was used by the Germans as a substitute for TNT.

The crystal density of Hexite is 1.653, and it can be pressed to a density of 1.60 when mixed with 1% of stearic acid and subjected to a pressure of 20,000 p.s.i. Its heat of combustion ( $\Delta H_p$ ) is 3001 cal./gram. Hexite is insoluble in water and is hygroscopic to the extent of only 0.09%. It is also insoluble in chloroform, is only slightly soluble in ether or cold acetic acid, but is readily soluble in acetone or warm acetic acid.

Chemically the compound acts as a pseudo acid. It is soluble in aqueous alkalis,

except potassium hydroxide, to form metallic salts. The potassium salt is insoluble in water.

Hexite can be prepared by the nitration of diphenylamine, *N*-methyldiphenylamine, or picryl-*p*-nitraniline (2,4,4',6-tetranitrodiphenylamine). The most practicable method of preparation consists of condensing aniline and 2,4-dinitrochlorobenzene to form 2,4-dinitrodiphenylamine, nitrating this with nitric acid (sp.gr. 1.33) at 50–60°C. to form 2,2',4,4'-tetranitrodiphenylamine, and nitrating this with mixed acid at ordinary temperature. Upon drowning the solution in ice water, the hexanitro compound is precipitated. It is purified by washing with water, dissolving in acetone, and precipitating with petroleum ether.

Hexite is only slightly less sensitive to impact than Tetryl, but is distinctly less sensitive to the impact of a rifle bullet or initiation by lead azide (Table IX). It is almost as brisant as Tetryl, as indicated by the sand test, and its rate of detonation (7100 m./sec. at sp.gr. 1.58) is somewhat less than that of Tetryl (Table X). The explosive power of Hexite is approximately 111% that of TNT and 86% that of Tetryl, as judged by the results of Trauzl lead block and ballistic pendulum tests. Its stability is of the same order as that of TNT and ammonium picrate (Table XI).

The overall toxicity of Hexite has not been extensively investigated, but it must be handled with care and its dust should not be inhaled because of its blistering action.

**TABLE IX. Sensitivity Characteristics of High Explosives.**

Explosive	Impact tests <sup>a</sup>		Pendulum friction test <sup>b</sup>	Rifle bullet test <sup>c</sup>	Explosion temp. test, °C. <sup>d</sup>	Detonating charge, min. grams		
	Test A, in.	Test B, cm.				Mercury fulminate	Lead azide	DDNP <sup>e</sup>
Ammonium nitrate...	31	—	0	0	—	<i>f</i>	<i>f</i>	—
Tetranitromethane...	—	100+	2	—	225	—	—	—
Ethylenedinitramine...	10	43	0	0	190	0.21	0.13	0.19
Nitroguanidine.....	—	47	0	0	275	<i>f</i>	—	0.72
Glycol dinitrate.....	< 2	56	7	—	257	—	—	—
Diethylene glycol dinitrate.....	2	100+	10	—	237	—	—	—
Nitroglycerin.....	—	15	10	10	222	—	—	—
Erythritol tetranitrate	—	10	—	—	225	—	—	—
PETN.....	6	17	5	10	225	0.17	0.03	0.09
DPIHN.....	4	14	10	—	255	—	0.18	—
MIIN.....	3	8	—	—	205	0.20	0.10	—
Nitrocellulose (13.3% N).....	—	10 (25)	—	—	230	—	—	—
Cyclonite.....	8	18	2	10	260	0.19	0.05	0.13
HMX.....	9	32	2	—	335	—	0.17	—
Dinitrobenzene.....	—	—	0	—	—	—	—	—
Trinitrobenzene.....	11	46	0	—	550	0.23	0.26	—
TNT.....	14	100	0	0.5	475	0.24	0.26	0.29
Picric acid.....	13	82	—	5	322	0.26	0.24	0.21
Ammonium picrate...	17	100+	0	1	318	<i>f</i>	<i>f</i>	0.27
Tetryl.....	8	26	0	7	257	0.19	0.10	0.17
Hexite.....	10	27	0	0	325	—	0.22	—

<sup>a</sup> Minimum fall of 2-kg. weight to cause at least 1 explosion in 10 trials.

<sup>b</sup> Steel shoe—number of explosions in 10 trials.

<sup>c</sup> Number of explosions in 10 trials.

<sup>d</sup> Temperature required to cause explosion in 5 seconds.

<sup>e</sup> Diazodinitrophenol test not the same as that using mercury fulminate or lead azide.

<sup>f</sup> Cannot be detonated completely in test with this initiator.

TABLE X. Explosive Characteristics of High Explosives.

Explosive	Sand test, grams	Rate of detonation		Trauzl lead block test, ml.	Ballistic pendulum test <sup>a</sup>	Produced by explosion: <sup>b</sup>	
		Density	M./sec.			Heat, cal./gram	Gas, ml./gram
Ammonium nitrate.....	—	0.9	1100-2700	165	—	346	980
Tetranitromethane.....	7.5	1.65	6400	155	—	—	—
Ethylenedinitramine.....	52.0	1.55	7750	—	136	1276	908
Nitroguanidine.....	36.8	1.55	7650	—	104	—	—
Glycol dinitrate.....	62.7	1.485	7300	600	—	1655	737
Diethylene glycol dinitrate..	47.5	1.375	6800	425	127	—	—
Nitroglycerin.....	58.7	1.60	7700	550	140	1478	713
Erythritol tetranitrate.....	62.5	—	—	—	—	1440	705
PETN.....	61.2	1.70	8300	500	145	1385	790
DPEHN.....	55.5	1.59	7410	380	—	1092	903
MHN.....	59.5	1.73	8260	520	—	1454	694
Nitrocellulose (13.3% N)....	50.8	1.20	7300	420	—	951	871
Cyclonite.....	59.0	1.70	8350	500	150	1300	908
HMX.....	54.4	—	—	450	150	—	—
Dinitrobenzene.....	25.5	1.50	6000	255	—	820	727
Trinitrobenzene.....	49.7	1.61	7440	325	110	1065	670
TNT.....	43.6	1.58	6900	295	100	925	730
Picric acid.....	47.9	1.70	7350	305	109	1000	675
Ammonium picrate.....	36.8	1.63	7150	—	98	800	—
Tetryl.....	54.0	1.71	7850	380	128	1120	760
Hexite.....	52.4	1.6	7150	320	113	1035	675

<sup>a</sup> TNT = 100.<sup>b</sup> Water produced in gaseous state at S.T.P.

TABLE XI. Stability Characteristics of High Explosives.

Explosive	Sample, grams	Vacuum stability test at:					
		100°C.		120°C.		150°C.	
		Mo.	Hr.	Mo.	Hr.	Mo.	Hr.
Ammonium nitrate.....	5.0	—	—	0.3	40	0.3	40
Ethylenedinitramine.....	5.0	0.5	40	1.5	40	11+	24
Nitroguanidine.....	5.0	0.4	40	0.5	40	—	—
Glycol dinitrate.....	1.0	0.7	8	0.7	8	—	—
Diethylene glycol dinitrate....	1.0	0.8	40	1.3	8	—	—
Nitroglycerin.....	1.0	11+	16	—	—	—	—
Erythritol tetranitrate.....	1.0	11+	16	—	—	—	—
PETN.....	5.0	0.5	40	11+	40	—	—
DPEHN.....	5.0	3.7	40	11+	16	—	—
MHN.....	1.0	11+	16	—	—	—	—
Nitrocellulose (13.3% N).....	5.0	0.9	24	11+	16	—	—
Cyclonite.....	5.0	0.7	40	0.9	40	2.5	40
HMX.....	5.0	—	—	0.4	40	0.6	40
Trinitrobenzene.....	5.0	—	—	1.0	40	—	—
TNT.....	5.0	0.1	40	0.4	40	0.7	40
Picric acid.....	5.0	0.2	40	0.5	40	—	—
Ammonium picrate.....	5.0	0.2	40	0.4	40	0.4	40
Tetryl.....	5.0	0.3	40	1.0	40	11+	12
Hexite.....	5.0	—	—	0.4	40	—	—

Use of a mixture of Hexite and TNT has been made under the name Hexanite, but this has been chiefly because of a TNT shortage. The ammonium salt of Hexite is readily prepared and is known as the dye Aurantia, which was used for silk and wool.

#### BINARY EXPLOSIVES

The first military binary explosive probably was the 60-40 picric acid - dinitrophenol mixture developed by the French to overcome the difficulties involved in the melt-loading of picric acid because of its high melting point. With the later development of TNT and the general shortage of this explosive in all countries during World War I, the ammonium nitrate - TNT mixtures termed Amatols were developed to utilize as far as possible the available supply of TNT. The sudden increase in the available TNT realized at the beginning of World War II rendered practical the development of new binary explosives. These were designed to utilize TNT as a carrier for more powerful explosives, rather than for economy in the use of TNT, and have the advantage of being suitable for melt-loading. Another development in the direction of binary explosives was the use of metallized explosives, such as the TNT-aluminum mixture termed Tritonal. These explosives have peculiarly pronounced blast effects and so are suitable for use in bombs.

**Amatols.** During World War I, 80-20 and 50-50 ammonium nitrate - TNT mixtures designated as 80-20 Amatol and 50-50 Amatol were used. The first of these is an essentially oxygen-balanced mixture about 75% as brisant as TNT, but it could not be melt-loaded and it was necessary to mix the hot materials so as to coat the nitrate crystals with molten TNT and load shell by the extrusion of the hot semiplastic mass. The 50-50 Amatol, however, is fluid enough to permit melt-loading in the same manner as TNT. During World War II, some 50-50 Amatol was used, particularly by the Germans, who had a limited supply of TNT.

50-50 Amatol is prepared by melting TNT and adding an equal weight of ammonium nitrate, which has been heated to remove surface moisture and prevent too rapid cooling of the TNT. The mixture is stirred, with some cooling, until the desired fluidity is obtained and then loaded directly into shell or bombs.

Cast 50-50 Amatol has a density of approximately 1.59 and detonates at a rate of 6400 m./sec. It is distinctly less brisant than TNT, as indicated by rate of detonation, fragmentation, and sand test values, but it has about 120% of the explosive power of TNT, as indicated by Trauzl lead block and ballistic pendulum tests. Although slightly more sensitive to impact than TNT, Amatol is of the same order of sensitivity to friction, as judged by pendulum friction and rifle bullet impact tests. It has a lower explosion temperature test value (265°C.) than TNT, but both are of the same order of sensitivity to initiation and stability. The heat of combustion ( $\Delta H_c$ ) of 50-50 Amatol is 2073 cal./gram.

**Tritonal.** A cast 80-20 TNT - flake aluminum mixture is termed Tritonal and has been used extensively in bombs because of its blast effect. The density of the cast explosive is 1.70-1.73, its rate of detonation is 6600 m./sec., and it is only 91% as effective as TNT in fragmenting shell. However, the explosive power of Tritonal is 124% that of TNT, as measured by the ballistic pendulum test. It is of the same order of sensitivity to impact and friction as TNT. As TNT and aluminum are not reactive, the stability of Tritonal is equal to that of TNT.

Tritonal is manufactured by melting TNT and then adding slowly, with mixing, the requisite quantity of flaked aluminum. After some cooling, the mixture of liquid

TNT, TNT crystals, and aluminum can be cast without segregation of the aluminum.

The effectiveness of Tritonal is ascribable to the large amount of heat liberated by the oxidation of the aluminum present; it is probable that at least some of this oxidation is accomplished by the oxygen of the air after detonation of the TNT and dispersal of the aluminum.

**Tetrytol.** A 70-30 Tetryl-TNT composition designated as Tetrytol has found use as a demolition explosive and bursting charge for mines because of its greater ease of initiation and brisance than TNT. It is prepared and melt-loaded in much the same manner as Tritonal.

Tetrytol has a density of 1.61-1.65 when cast, and so permits the use of a slightly greater weight of charge than of TNT. Its rate of detonation, 7350 m./sec., is distinctly greater than that of cast TNT, and this is reflected by its greater brisance and fragmentation efficiency. Its explosive power is 120% that of TNT.

As indicated by rifle bullet impact tests, Tetrytol is very slightly more sensitive than TNT. Its stability, as measured by 100 and 120°C. vacuum stability tests, is slightly less than that of Tetryl. However, with a melting point of only 68°C., it has been found to withstand storage at 65°C. for 2 years and is of satisfactory stability from a practical viewpoint.

**Pentolite.** A number of PETN-TNT mixtures, known as Pentolites, have been used. Of these the 50-50 mixture is of the greatest importance in the loading of ammunition; it is used as a bursting charge for grenades and as a booster-surround charge because of its sensitivity to initiation and great brisance.

Pentolite is manufactured by coprecipitating PETN and TNT or by adding wet PETN to molten TNT and heating until the moisture is driven off. Dry Pentolite can be pelleted for use in detonators, boosters, etc.

Cast Pentolite has a density of 1.63-1.67. It is one of the most sensitive military explosives, as indicated by the rifle bullet impact test, and is much more sensitive to initiation than Tetrytol. Its rate of detonation (7450 m./sec.) is essentially that of Tetrytol, and its brisance is approximately that of Tetrytol, but the explosive power of Pentolite is significantly greater than that of Tetrytol.

The stability of Pentolite is indicated by vacuum stability tests to be slightly less than that of PETN. However, Pentolite undergoes no marked deterioration during storage at 65°C. for 2 years and withstands ten remelting operations without becoming unstable or unduly acid. It is, therefore, considered to be of satisfactory stability, although it is not as stable as most of the other military explosives.

**Picratol.** As some types of ammunition, such as armor-piercing projectiles, require the use of an explosive that is relatively insensitive to impact, and the castability of bursting charges is an imperative requirement, a mixture of approximately equal weights of TNT and ammonium picrate, designated as Picratol, has been used. This is much less sensitive than TNT, has a slightly higher density (1.62), has practically the same rate of detonation, and has the same fragmentation efficiency as TNT. It is of the same high order of stability as both TNT and ammonium picrate. Picratol is manufactured and loaded in the same manner as Tetrytol.

**Cyclotol.** Because of its great brisance and blast effects, a 60-40 Cyclonite-TNT composition was used during World War II as a bursting charge for bombs.

Cyclotol has a density of 1.65-1.70. It is about as insensitive to frictional impact as TNT, but is much more sensitive to initiation. The rate of detonation of Cyclotol (7800 m./sec.) is greater than that of any other binary explosive used for melt-loading



bombs, and its fragmentation efficiency is correspondingly greater than that of TNT. Ballistic pendulum tests indicate it to have 130% the explosive power of TNT, and it has a markedly greater blast effect than TNT.

Vacuum stability test values show Cyclotol to be at least as stable as Cyclonite and to be chemically unchanged after storage at 65°C. for 1 year.

Cyclotol is manufactured by adding moist Cyclonite to molten TNT and heating until the moisture has been removed by evaporation. In some cases 1% of wax that can be dispersed in the molten TNT is added. This serves to increase the density and uniformity of the cast explosive and causes very slight desensitization to impact.

**Liquid Binary Explosives.** Originating in the oxidizer-reducer mixtures invented in 1871 by Sprengel, a number of liquid binary explosives have been proposed that have been used to a limited extent but have serious practical disadvantages.

**Anilite**, a mixture of 60% nitrogen dioxide and 40% aniline, is so sensitive that the ingredients must be kept separate until the last moment. Other mixtures of nitrogen dioxide with toluene, nitrobenzene, etc., are similarly sensitive. Mixtures of fuming nitric acid with picric acid, nitrobenzene, etc., have been used to a limited extent, and are less sensitive than the Anilites; however, the dangerously corrosive action of nitric acid makes such use difficult. Mixtures of tetranitromethane with toluene, nitrotoluene, etc., are extremely powerful, but they become increasingly sensitive as their stoichiometric proportions are approached and are considered extremely hazardous to use.

**Chlorate and Perchlorate Binary Explosives.** Many efforts have been made in industry to apply solid binary explosives of the Sprengel type, but this has not resulted in pronounced success because of the dangerous sensitivity of such mixtures. A simple mixture of sugar and potassium chlorate is dangerously sensitive to friction and has caused serious injury to unwarned students attempting its preparation. Rack-a-Rock, a 79-21 mixture of potassium chlorate and nitrobenzene, was once used extensively but has long been abandoned.

Attempts to overcome undesirable sensitivity to friction led to the substitution of potassium perchlorate for the chlorate and the desensitization of the chlorate by means of castor oil. These efforts led to further complications of the compositions, and this type of blasting explosive no longer could be considered as a binary explosive. In spite of these repeated efforts to render the explosives safe to manufacture, disastrous explosions generally have terminated such efforts; and, today, they are of relatively little importance.

#### PLASTIC EXPLOSIVES

This type of explosive may be considered to be an outgrowth of the "waxing" of explosives so as to render them more suitable for pelleting and press-loading in detonators, etc.

The admixture of approximately 1% of stearic acid or other waxy material with Tetryl has long been utilized, although this was recognized to cause some slight desensitization of the explosive to initiation as well as friction.

With the relatively recent development of the more sensitive explosives PETN and Cyclonite, it was found that small quantities of these could be press-loaded in detonators and shell if the proportion of wax was increased to 10% or even more. Such compositions may be considered semiplastic. Explosive compositions of this type can be manufactured by mixing the explosive and powdered wax in a tumbling barrel.

New tactical requirements during World War II resulted in the hasty development of truly plastic explosives, used chiefly for demolition purposes. Previously,

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hard blocks of TNT, Tetrytol, or a nitrostarch explosive had been used for demolition purposes. The new requirements were for explosives that could be molded easily by hand so as to conform to the surface of an object or be suitable for tamping into cavities. A putty-like material not changed appreciably by changes in temperature might be considered optimum.

Because of its outstanding sensitivity, brisance, and stability characteristics, Cyclonite generally has been the basic explosive of the plastic explosives, although PETN has been used to some extent.

An 88-12 Cyclonite-lubricating oil mixture is an example of a simple plastic explosive, but is somewhat lacking in cohesiveness and resistance to changes in temperature. A more suitable mixture is a 77-23 mixture containing a plastic binder composed of nitro aromatic compounds and a small percentage of nitrocellulose. This composition is more cohesive, but it is more toxic and may undergo some segregation of binder during storage at high temperatures.

The recently developed plastic explosives may be considered as far-from-perfect examples of a type of explosive that probably will undergo extensive development in the future.

### BLASTING EXPLOSIVES

Blasting explosives, often referred to as commercial explosives to distinguish them from military explosives, represent explosives that have such characteristics of strength, resistance to water, safety in transportation and in use, and low cost of manufacture, as to make them satisfactory for general use as blasting agents.

Black powder was the earliest commercial explosive and for many years was the only mining explosive known. When nitroglycerin was first discovered, its great strength and particularly its very quick explosive action, as distinguished from the much slower explosive action of black powder, promptly led to its use in the excavating of tunnels in hard rock. Many accidents followed the early efforts to manufacture nitroglycerin, and many more accidents followed the early efforts to transport and use this powerful but very sensitive explosive. The invention by Nobel of dynamite (patented in 1867) and of blasting gelatin (patented in 1875) represent important milestones in the development of mining explosives; up to the present day, explosives of the general type developed by Nobel, although they have been greatly improved over the years, still represent highly efficient and satisfactory blasting explosives.

The requirements of an explosive satisfactory for general blasting use are exacting. The explosive must possess sufficient sensitivity to ignition (in the case of black blasting powder) or detonation (in the case of other blasting explosives) to enable it to be exploded without failure, while it must be sufficiently insensitive to ignition, explosion, or detonation to enable it to be transported and handled with reasonable safety. It must be capable of withstanding prolonged storage without deterioration through the cold of winter and the heat of summer, and must be certain to function properly over a wide range of temperature. The explosive should be capable of being handled by relatively inexperienced workmen; however, it should be recognized that every explosive represents concentrated energy ready to be evolved in a very tiny fraction of a second when subjected to certain conditions and that, therefore, no explosive can be made that will be proof against accidents when it is carelessly handled or improperly used.

Other factors, such as good shattering strength, good heaving or pushing strength,

low cost, satisfactory physical consistency, good resistance to water, and the production on detonation of a minimum of noxious fumes, may be considered as special characteristics of certain types of explosives, but reasonable safety in transportation, handling, and use is a general characteristic that every commercial blasting explosive must possess.

By suitable formulation it is possible to make explosives having flame temperatures so low and so short in duration that they can be used with relative safety (in not greater than certain prescribed quantities and according to certain prescribed methods) in coal mines in the presence of gas and coal dust. These explosives are known generally as "low-flame-temperature" explosives, and those that have passed the prescribed tests of the U.S. Bureau of Mines for explosives for use in coal mines are known as "permissible" explosives.

By suitable formulation it is also possible to make explosives having so high a sensitivity to a propagated shock wave that rows of holes filled with such explosive and spaced not too far apart can be fired without separate initiation by a detonator of the explosive in each individual hole. Such explosives are much used in ditching.

Other explosives formulated for highly specialized uses are applied to oil-well blasting, seismic prospecting, stumping, logging, etc. Each of these special types of explosives has been formulated to meet some specific requirement, and often this involves undesirable changes in other characteristics. Thus, an explosive formulated to have high sensitivity for ditching purposes must of necessity be somewhat more sensitive to shock than most other types and must, therefore, be handled more carefully. Explosives specially formulated for low sensitivity and an exceptionally high degree of safety require the use of a stronger detonator than is needed for explosives of normal type.

The formulation of explosives is a highly developed science which has resulted in the development of blasting explosives that are quite safe in manufacture, transportation, and use and that develop their strength in the particular way best adapted to the needs of the special use for which they are formulated.

Although many efforts have been made to develop chlorate and perchlorate explosives, these explosives are at present manufactured in such relatively small amounts that they will not be considered here as blasting explosives. It is possible that satisfactory chlorate or perchlorate explosives for general blasting use may be developed in the future, but up to the present time their tendency toward erratic sensitivity and their formation of acrid and annoying fumes has limited their production to such a point that their present manufacture as commercial explosives in the U.S. is negligibly small.

### **Black Blasting Powder**

Black blasting powder is essentially similar in composition to the potassium nitrate black powder used for military purposes:  $72 \pm 2\%$  sodium nitrate;  $16 \pm 1\%$  charcoal;  $12 \pm 1\%$  sulfur. The higher oxygen content of sodium nitrate as compared with potassium nitrate permits the use of less nitrate than is present in potassium nitrate black powder.

The manufacture of black blasting powder is the same as that described for military black powder (see p. 3). The graphite-glazed grains are sieved to sizes designated as CCC, CC, C, F, FF, FFF, and FFFF. The average diameter of the CCC granulation is about 14 mm., while that of the finest or FFFF granulation is 1–2 mm.

Black blasting powder is produced also in the form of cylindrical pellets having central perforations. Several such pellets may be wrapped together to form a cartridge of desired diameter and length. Pelleted black blasting powder contains some starch as a partial replacement for charcoal; the starch is added to the mix in the form of a paste. While it is practicable to make pellets from the mix as it comes from the wheel mill, generally a "press cake" is made and granulated before the pellets are made. The moisture remaining in the pressed pellets is removed by drying on trays before cartridges are made up. Pelleted black powder is produced in several "grades," which differ in density and, therefore, in burning rate. In recent years, the sales of pelleted powder have exceeded those of granulated black blasting powder. The greatest use of such powder is in coal mining; pelleted powder has been found to give the better breakage of coal under some conditions. Granulated black blasting powder has a density of approximately 1.8, but that of pelleted powder is only 1.35–1.50.

Black blasting powder has very little shattering power, but exerts a strong heavy-ing or pushing effect. It is particularly satisfactory for blasting soft materials, where the much more rapid explosion of dynamite is unnecessary and gives less satisfactory results.

Confinement at the moment of explosion increases the effectiveness of all explosives, and this is particularly true of black blasting powder. The "stemming" of holes loaded with black powder is necessary in order to obtain any significant blasting effect. Tests with different quantities of stemming material have shown increased effectiveness up to the point where that portion of the borehole not loaded with powder is completely filled with stemming.

The products of explosion of black blasting powder are similar to those produced by potassium nitrate black powder except that sodium compounds are formed. The heat and gas volume values of the two types of black powder are approximately equal.

### Dynamite

Alfred Nobel found that by absorbing nitroglycerin in a porous mineral earth called kieselguhr he obtained a mixture, which he called dynamite, that was free from some of the disadvantages of liquid nitroglycerin; he was granted a British patent on this invention in 1867. The kieselguhr, or impure diatomite (*q.v.*), was chemically inert and contributed nothing to the reaction that occurred when the nitroglycerin was detonated; however, the loosely coherent solid that was produced by absorbing nitroglycerin in the porous earth was much easier and safer to handle than liquid nitroglycerin and was quickly accepted by users who had been reluctant to handle liquid nitroglycerin.

The first dynamites were graded by the amount of nitroglycerin that was present in the mixture, so that the product obtained by mixing 60 parts of nitroglycerin and 40 parts of kieselguhr was called "60% dynamite," and all other mixtures were graded in a similar way.

It was not long before it was found that by substituting other materials for kieselguhr still stronger explosives could be made. For example, by employing a mixture of finely ground sodium nitrate and a combustible material such as wood pulp as the absorbent, instead of the inert kieselguhr, an explosive was obtained that was materially stronger than the earlier dynamite containing exactly the same amount of nitroglycerin.

Explosives so formulated were known as "active-dope" dynamites, to distinguish them from the earlier dynamites that contained only inert absorbent, and promptly replaced the latter. It has now been many years since inert-dope dynamites (guhr dynamites) have been made in the U.S., although they are still made abroad to some extent, and the term "straight" dynamite, as used today, can be taken as referring to an active-dope dynamite.

A number of years after nitroglycerin dynamites were first made, dynamites employing nitrostarch instead of nitroglycerin were made; the term "dynamite," which at first was used to designate only nitroglycerin explosives, became a generic term for high explosives used industrially in engineering and mining work incident to quarrying stone, sinking shafts, driving tunnels, and other surface and underground blasting operations.

*Ammonia dynamites* or *ammonium nitrate dynamites* contain substantial amounts of ammonium nitrate, which usually replaces part of the nitroglycerin or other sensitizing agent and also part of the sodium nitrate. To the extent that ammonium nitrate replaces sodium nitrate in a dynamite, it tends to increase the gas produced by the explosive. The ammonium nitrate explosives are very widely used; most blasting explosives of high heaving effect or pushing force contain substantial amounts of ammonium nitrate.

In 1875 Nobel disclosed another way of making solid explosives from liquid nitroglycerin by utilizing the colloidizing action of nitroglycerin on nitrocellulose. This was based on the use of nitrocellulose (collodion) having a nitrogen content of about 12%, which is converted by nitroglycerin into a jellylike mass. When low percentages of soluble nitrocellulose are used, the effect is merely to increase the viscosity of the nitroglycerin; but, when mixtures of 88-92 parts of nitroglycerin and 12-8 parts of soluble nitrocellulose are made, a tough product results. This product is known as *blasting gelatin*; since it consists wholly of explosive ingredients of high explosive strength, it is a particularly strong blasting explosive.

By including some nitrocellulose in the compositions of ordinary active-dope dynamites, the so-called "*gelatin dynamites*" are obtained. These are characterized by their greater density and resistance to water than straight active-dope dynamites containing sodium nitrate or small amounts of ammonium nitrate.

Although dynamites of a nitroglycerin base and dynamites of a nitrostarch base are similar in appearance and in their general explosive characteristics, they are not identical in all respects. Nitrostarch, as used in explosives, is a pulverulent solid material that cannot freeze at atmospheric temperatures as does nitroglycerin. It is also free from the tendency to produce headache when an explosive containing it comes in contact with the unprotected skin or when small amounts of muck-pile gases (gases remaining after an explosion) are inhaled.

The addition of "antifreeze" materials, such as nitrotoluene, nitrated diglycerin, nitrated sugars, and the nitroglycols, so greatly reduces the tendency of nitroglycerin to freeze that the earlier necessity of thawing nitroglycerin explosives that had been exposed to low temperatures has been substantially eliminated. In formulas for dynamites, it is customary to consider as nitroglycerin both nitroglycerin itself and the antifreeze materials that are associated with it. Sugars, glycols, diglycerin, etc., are usually added to glycerin before it is nitrated, and thus are nitrated with it as a part of its manufacture.

## STRAIGHT DYNAMITES

The straight dynamites may be considered as standards of reference in comparing the strength of other types of dynamite: the percentage of nitroglycerin present corresponds to the rated strength of the dynamite. Thus, for example, 40% straight nitroglycerin dynamite contains 40% of nitroglycerin; 60% straight nitroglycerin dynamite contains 60% of nitroglycerin; etc.

Low-freezing straight dynamites contain antifreeze materials that have slightly less explosive strength than nitroglycerin, so that the actual amount of the nitroglycerin or nitroglycerin equivalent in a low-freezing straight dynamite may differ somewhat from the rated percentage strength.

That portion of a straight dynamite that is not represented by the organic nitrate detonable constituent or constituents is usually a mixture of: a good grade of wood pulp, or other carbonaceous material, the purpose of which is to absorb the liquid nitroglycerin or mixture high in nitroglycerin; sodium nitrate to supply available oxygen to the carbonaceous material; and calcium carbonate, zinc oxide, or other antacid material to neutralize any traces of acidity that may be produced by decomposition of any of the organic nitrates present.

It is desirable that the wood pulp or other combustible absorbent material and the sodium nitrate or other oxidizing material should be present in balanced proportions; enough of the nitrate should be present to oxidize completely the combustible, carbonaceous, absorbent material. If too much inorganic nitrate is present, the explosive tends to evolve nitrogen oxides in the products of explosion, and does not liberate as much energy as it would if the proportions were balanced. The presence of too much of the combustible absorbent agent leads to the presence of excessive amounts of carbon monoxide in the gases produced on explosion. The presence of large amounts of either carbon monoxide or nitrogen oxides in the explosive gases is undesirable, particularly when the dynamite is used in underground mining work. In some states, legislation has been enacted classifying explosives into certain "fume" groups, depending upon the amount of noxious gases, particularly carbon monoxide, hydrogen sulfide, and nitrogen oxides, produced when the explosive is detonated under prescribed test conditions.

It is to be noted that the wrapper of the explosive forms a part of the chemical mixture involved in the reactions that occur on the detonation of the explosive; accordingly, this factor is also taken into consideration in the formulation of dynamites of all types. A small additional percentage of sodium nitrate is used in the explosive formula so that the entry of the paper and paraffin of the wrapper into the reaction will not too greatly increase the amount of carbon monoxide produced on explosion. Table XII gives the compositions of typical straight dynamites.

The straight dynamites are characterized by a relatively high rate of detonation, which increases as the amount of nitroglycerin present in the formula increases. They also have good gas volumes.

The straight dynamites were formerly used extensively in mining and quarrying; their principal use was in rock that was hard and tough, but not sufficiently tough to require use of blasting gelatin or the gelatin grades of dynamite. Since the cost of straight dynamites is somewhat higher per unit of strength than other explosives that give substantially equal results in blasting, their use in recent years has been largely supplanted by "ammonia dynamites" and "ammonia gelatin dynamites," and they are no longer made regularly (except on order) by most explosive manufacturers in the U.S.

## AMMONIA DYNAMITES

In the ammonia dynamites, ammonium nitrate is used to replace a portion of the organic nitrate detonable constituent, so that the amount of nitroglycerin or other organic nitrate detonable constituent used in the formula is considerably lower than the rated strength of the explosive. Since ammonium nitrate has less explosive strength than nitroglycerin, it is necessary to use more ammonium nitrate in a formula than the amount of nitroglycerin that it replaces.

The other constituents of ammonia dynamites are in general the same as in the straight dynamites, although a slightly larger amount of antacid is usually employed because experience has indicated that mixtures of ammonium nitrate and nitroglycerin tend to produce acidity somewhat more readily than do mixtures of sodium nitrate

TABLE XII. Compositions of Typical Dynamites.

Constituent	Strength of dynamite						
	20%	30%	40%	50%	60%	80%	100%
A. Straight dynamites							
Moisture, %.....	0.9	1.0	0.9	0.9	1.2	—	—
Nitroglycerin, %.....	20.2	29.0	39.0	49.0	56.8	—	—
Sulfur, %.....	2.9	2.0	—	—	—	—	—
Sodium nitrate, %.....	59.3	53.3	45.5	34.4	22.6	—	—
Antacid, %.....	1.3	1.0	0.8	1.1	1.2	—	—
Carbonaceous combustible material, %	15.4	13.7	13.8	14.6	18.2	—	—
B. Ammonia dynamites							
Moisture, %.....	0.8	0.8	0.7	0.9	0.7	—	—
Nitroglycerin, %.....	12.0	12.6	16.5	16.7	22.5	—	—
Sulfur, %.....	6.7	5.4	3.6	3.4	1.6	—	—
Ammonium nitrate, %.....	11.8	25.1	31.4	43.1	50.3	—	—
Sodium nitrate, %.....	57.3	46.2	37.5	25.1	15.2	—	—
Antacid, %.....	1.2	1.1	1.1	0.8	1.1	—	—
Carbonaceous combustible material, %	10.2	8.8	9.2	10.0	8.6	—	—
C. Gelatin dynamites <sup>a</sup>							
Moisture, %.....	0.9	1.0	0.9	1.0	0.9	0.7	0.1
Nitroglycerin, %.....	20.2	25.4	32.0	40.1	49.6	65.4	91.0
Nitrocellulose (soluble), %.....	0.4	0.5	0.7	0.8	1.2	2.6	7.9
Sulfur, %.....	8.2	6.1	2.2	1.3	—	—	—
Sodium nitrate, %.....	60.3	56.4	51.8	45.6	38.9	19.5	—
Antacid, %.....	1.5	1.2	1.2	1.2	1.1	1.7	0.8
Carbonaceous combustible material, %	8.5	9.4	11.2	10.0	8.3	10.1	—
D. Ammonia gelatins							
Moisture, %.....	—	1.5	1.4	1.6	1.7	1.8	—
Nitroglycerin, %.....	—	22.9	26.2	29.9	35.3	38.3	—
Nitrocellulose (soluble), %.....	—	0.3	0.4	0.4	0.7	0.9	—
Sulfur, %.....	—	7.2	5.6	3.4	—	—	—
Ammonium nitrate, %.....	—	4.2	8.0	13.0	20.1	34.7	—
Sodium nitrate, %.....	—	54.9	49.6	43.0	33.5	19.1	—
Antacid, %.....	—	0.7	0.8	0.7	0.8	0.9	—
Carbonaceous combustible material, %	—	8.3	8.0	8.0	7.9	4.3	—

<sup>a</sup> The 100% member of the gelatin dynamite series is blasting gelatin.  
Source: reference (20).



and nitroglycerin (see Table XII). The increase is not large, however, and rarely exceeds 0.1 or 0.2%.

The ammonia dynamites represent one of the most generally used types of mining and quarrying explosives. Although ammonia dynamites are somewhat less water-resistant than the straight dynamites and materially less water-resistant than the gelatin dynamites, they have sufficient water resistance for most mining and quarrying purposes. They have excellent strength characteristics, both in the vigor of the blow that they deliver at the instant of detonation (brisance) and in the sustained pressure and heaving or pushing action that follow the striking force (gas volume). Since the ammonia dynamites are somewhat cheaper than other grades of explosives, not only on the "per pound" basis, but also on the basis of the actual amount of energy that they deliver, they have become one of the most favored of blasting explosives for ordinary mining and quarrying purposes.

#### BLASTING GELATIN AND THE GELATIN DYNAMITES

Blasting gelatin consists of nitrocellulose of about 12% nitrogen content colloided with nitroglycerin to form a rather tough gel. Although the percentage of soluble nitrocellulose used by different manufacturers varies slightly because the colloid characteristics of nitrocellulose in turn depend upon its nitrogen content, the usual relationship is about 11.5 parts of nitroglycerin to 1 part of soluble nitrocellulose. The only other constituent of blasting gelatin is a small amount of an antacid material such as calcium carbonate, magnesium carbonate, or zinc oxide.

The gelatin dynamites may be thought of as a series of explosives of which blasting gelatin is the "100%" member, and each of the other gelatin dynamites represents an admixture of somewhat less gelatinized nitroglycerin and an active dope that has been formulated to give a balanced reaction on explosion. In the gelatin dynamites of lower rated strength, sulfur is often used as a component of the "active dope" (see Table XII).

The gelatin dynamites are characterized by high density and excellent resistance to water. They are strong explosives, with good gas volume and brisance values. Their largest use at present is in submarine operations and seismic prospecting work, where the cartridges may at times remain submerged under water for such prolonged periods that other explosives would tend to absorb enough water to interfere with their complete explosion. In recent years, the ammonia gelatin dynamites have largely replaced the straight gelatin dynamites in mining and quarrying use, as they are somewhat less sensitive to detonation and exert a somewhat greater proportion of their explosive strength as pushing or heaving force, while still having sufficiently high rates of detonation for most of the work in which the straight gelatin dynamites have been used.

**Ammonia gelatin dynamites** are formulated to combine, as far as is possible, the best characteristics of the gelatin dynamites and the ammonia dynamites. They consist essentially of an ammonia dynamite in which the nitroglycerin is present in the form of a nitrocellulose colloid (see Table XII). They do not have resistance to water equal to that of the gelatin dynamites, but they are more resistant to water than the ammonia dynamites. In gas volume and heaving or pushing effect, they are superior to the gelatin dynamites but are slightly inferior to the ammonia dynamites.

**Semi-gelatin dynamites** are intermediate in composition between the ammonia gelatin dynamites and the ammonium nitrate dynamites, and are essentially ammo-

nium nitrate dynamites to which has been added insufficient nitrocellulose to form a stiff gel. Physically, semi-gelatin dynamites are more plastic than the ammonia dynamites; they are in general somewhat less sensitive in friction and shock tests than the gelatin dynamites. However, their sensitivity is sufficient to insure their satisfactory response to the action of a standard detonating charge.

### Ammonium Nitrate Explosives

Ammonium nitrate is an important constituent of ammonia dynamites, but it is also the significant constituent in a number of other explosives in which it is present in substantially larger proportions than in the ammonia dynamites. These ammonium

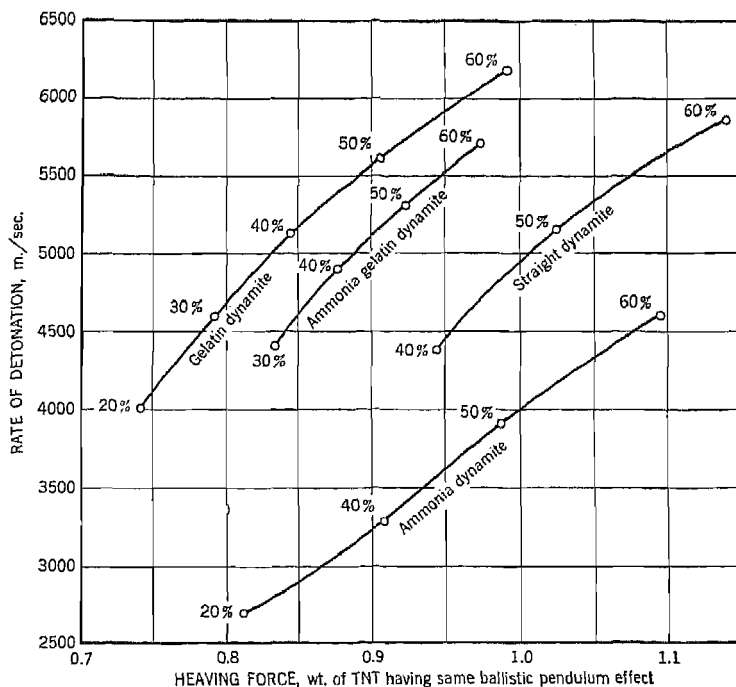


Fig. 1. Approximate detonation rates and heaving forces of various dynamites.

nitrate explosives are of two somewhat different types: (1) explosives in which a sensitizer that is itself detonable is used as the means of increasing the sensitivity to detonation of the ammonium nitrate, and (2) explosives in which the material that is employed to sensitize the ammonium nitrate is not itself detonable.

Ammonium nitrate explosives are generally characterized by a low rate of detonation and a high gas volume, which would be expected to result in low shattering effect and good heaving or pushing effect. In use in quarries, it has been found that ammonium nitrate explosives often show a shattering effect greater than would be expected from their relatively low rate of detonation, and this is ascribed to the large volume of their gaseous products of explosion having a disproportionate effect on shattering power. As ammonium nitrate explosives are rarely graded commercially in percentage strength, it would be difficult to plot their strength in Figure 1; however, in gen-

eral, they are considered in the trade as being of "65% weight strength." Most of them have rates of detonation within the range 2000–3500 m./sec., and in the ballistic pendulum test many of them have an effect equal to that of 1.15–1.25 times as much TNT. This means that these explosives, although they have a much lower rate of detonation than TNT, may on explosion produce a greater heaving or pushing effect.

**Ammonium Nitrate Explosives Containing Detonable Sensitizers.** There is no sharp line of division between the ammonia dynamites and some ammonium nitrate explosives; the difference is mainly that ammonium nitrate explosives are formulated with a lower percentage of nitroglycerin or nitrostarch and the percentage of ammonium nitrate in the formula is increased. The presence of as little as 1% of nitroglycerin or nitrostarch in ammonium nitrate is sufficient to produce marked sensitization, and commercial ammonium nitrate explosives are made by using from 3 to 10% nitroglycerin or nitrostarch as a sensitizer and from 40 to more than 80% ammonium nitrate. The remainder of these explosives is usually a small amount of wood pulp or other carbonaceous material (in the case of ammonium nitrate explosives sensitized by nitroglycerin) and the usual antacid constituents.

TNT, nitrotoluenes, nitronaphthalenes, and many other similar materials have been patented or suggested as sensitizers for ammonium nitrate explosives, and some of them have come into wide commercial use, particularly in foreign countries. However, in the U.S., nitroglycerin and nitrostarch are the principal detonable sensitizers used in the formulation of this type of ammonium nitrate explosive.

**Ammonium Nitrate Explosives Containing Nondetonable Sensitizers.** There are a large number of materials which are not themselves explosives, but which, when added to ammonium nitrate, greatly increase its sensitivity.

Effective sensitizers for ammonium nitrate may be inorganic materials such as powdered metals and, particularly, flake aluminum, or they may be combustible organic materials, of which the number of relatively efficient sensitizers is very great. Rosin and many of the metallic resinates, hexamethylenetetramine and many organic bases, and paraffin oils and waxes are among the very large number of materials that have been found to act as efficient sensitizers of ammonium nitrate.

An interesting type of ammonium nitrate explosive sensitized by a nondetonable sensitizer employs ammonium nitrate (alone or admixed with sodium nitrate or other materials) in the form of granules, with the sensitizer present as a thin coating or film on these granules. Explosives of this type detonate from the action of standard detonators and are strong and efficient explosives.

Another interesting type of ammonium nitrate explosive employs an amount of sensitizer insufficient to make the explosive capable of detonation from the action of an ordinary blasting cap, although it may be detonated by a materially heavier initiating charge. By the use of heavy "booster charges" (usually of TNT or Amatol, which is ammonium nitrate sensitized by TNT), these explosives of low sensitivity can be caused to detonate completely. Their exceptional safety, because of the fact that the explosive itself is incapable of detonation in the absence of the booster charge, has led to their extensive and successful use. A mixture of 92.5% ammonium nitrate, 4.0% dinitrotoluene, and 3.5% paraffin wax is representative of this type of explosive. By regulation of the density, bulk strengths between 40 and 75% are available, based on straight dynamite. The velocity varies with grade and diameter, and is generally between 3500 and 5000 m./sec. When properly initiated, the explosion can be propa-

gated across air gaps up to 5-18 in. In order to exclude moisture, the material is packed in sealed metal cans.

### Low-Flame-Temperature and "Permissible" Explosives

The ignition of a combustible mixture requires time; even such combustible systems as a mixture of flammable gas and air, or a suspension of coal dust in air, require for ignition a temperature greater than a certain minimum and the maintenance of this temperature for a very short but measurable period of time (see *Explosions*). Explosives can be formulated so that the maximum temperature of the reaction developed during explosion is relatively low and of short duration. It is thus practicable to produce coal-mining explosives that, when fired under prescribed conditions of loading and weight of charge used, are substantially free from the danger of igniting such mixtures of flammable gas and air as are sometimes met with in coal mines and such suspensions of coal dust in flammable mixtures of gas and air as may be stirred up in the mine when a shot "cannons" or blows out through the borehole instead of pulling the burden of coal properly. Explosives of low flame temperature are called "permissible" explosives when they are so classified by the U.S. Bureau of Mines after having passed a series of special and carefully controlled tests.

There are a number of ways in which explosives of low flame temperature may be produced. In general, this is done by either: formulating the explosive so that the explosive reactions are not strongly exothermic; or adding to the explosive composition materials which may be inactive as a part of the explosive reactions, but which have a high capacity for heat.

The explosive reaction between oxygen and carbon that results in the formation of carbon dioxide is highly exothermic; however, when sufficient carbon is present so that its oxidation results in the formation of carbon monoxide instead of carbon dioxide, the maximum temperature produced by the reaction is materially lowered. This means that by increasing the carbon that is present in any explosive formula so that more carbon monoxide and less carbon dioxide appear in the products of explosion, the flame temperature produced by that explosive will be reduced. The production of excessive amounts of carbon monoxide has, of course, undesirable aspects, but modifying the explosive reaction so as to decrease the carbon dioxide produced and correspondingly increase the carbon monoxide represents a very effective means of reducing flame temperature.

The presence in an explosive of any material that will absorb heat during the explosive reaction represents another way of reducing the flame temperature, and finely divided inert materials such as diatomite, powdered slate, and clay may be used for this purpose. More effective are materials that volatilize at the temperature produced by the explosive reaction, such as free water; water of crystallization in salts such as magnesium sulfate, the alums, and calcium sulfate; and salts that are themselves volatile at the temperature of the reaction, such as sodium chloride.

Instead of incorporating temperature-reducing constituents in the explosive itself, explosive assemblies have been made (particularly in Germany, England, and Belgium) that comprise an inner explosive cartridge surrounded by an annular layer or "sheath" of a mixture that has flame-reducing properties. The primary explosive should be a composition that itself produces on detonation only a relatively low explosion temperature. As a surrounding sheath, a mixture of 15 parts of nitroglycerin, 50

parts of sodium bicarbonate, and 35 parts of sodium chloride has met with wide acceptance in Germany.

In the manufacture of sheathed cartridges, the outer cartridge wrapper is rolled by a machine that fills it with the sheathing composition; a cylindrical cutter removes the sheathing composition from the portion of the cartridge that is to be filled by the explosive cartridge, which is then inserted. The portion of the sheathing composition that is scooped out by the cutter member is re-used.

### **Liquid Oxygen Explosives**

Liquid oxygen explosives (L.O.X.) are mechanical mixtures of a combustible absorbent material (usually carbon black, lampblack, or the like) and liquid oxygen. The carbon or carbonaceous material is contained in cartridges, which are usually made of either paper or cloth, and the cartridges so prepared are immersed in liquid oxygen of 95% or higher purity shortly before the explosive is to be used.

After sufficient time has been allowed to permit the liquid oxygen to impregnate the porous combustible material, the cartridge is removed from the impregnating vessel. From the moment of removal the oxygen begins to evaporate, and, accordingly, the cartridge must be used within a short time after it has been impregnated with the liquid oxygen. The length of time required to impregnate the cartridge and the length of time that can elapse between the time the cartridge is removed from the impregnating bath and the time it is fired both depend largely upon the diameter of the cartridge. With cartridges of small diameter, the time allowed for impregnation may be from 15 to 30 minutes, and the cartridges should be fired within 15 minutes of the time they are removed from the soaking box. With cartridges of from 5- to 8-in. diameter, a soaking period of from  $\frac{1}{2}$  to 1 hour is usually allowed, and the cartridges should be used within 45 minutes of the time they are removed from the soaking box. Electric detonators are used in firing small charges of L.O.X., and large blasts may be fired by the use of either electric detonators or Primacord (detonating fuse loaded with PETN).

Maximum effect is produced when the weight relationship between liquid oxygen and the porous carbonaceous combustible material is stoichiometric; this relationship exists only for a very short period of time, since before the optimum moment the oxygen is in excess and after the optimum time the carbonaceous material is in excess. For successful use the cartridge should be fired within a few minutes of the moment when it has the composition that gives maximum explosive strength.

It is claimed that L.O.X. can be made at a lower cost per pound than that of fixed explosives; but actual blasting costs when L.O.X. are used are usually reasonably close to the corresponding cost when fixed explosives are used. The disadvantage of L.O.X. is that for maximum economy the liquid oxygen plant must run continuously, and accordingly the usage of explosives must not only be reasonably continuous, but also the amounts used each day must not vary widely. L.O.X. have been used successfully in a few large mining and stripping operations, where the demand for explosives is both steady and continuous, but for other work their use has been less successful. L.O.X. are generally believed to be somewhat more liable to accidental explosions than are the fixed explosives; however, it should be remembered that in the early years of the use of fixed explosives many more accidents occurred from their use

than occur at present. Much research is being done in an effort to make L.O.X. safer than they are at present.

Extensive experiments by the U.S. Bureau of Mines indicated that L.O.X. have rates of detonation varying from less than 4000 up to 6200 m./sec., the actual rate depending upon the nature of the carbonaceous material used and the exact ratio between liquid oxygen and carbonaceous material that exists at the moment of detonation. The conclusion was reached that these explosives under favorable conditions show about the same explosive strength that is shown by 40% dynamite. The best absorbents for the liquid oxygen appear to be carbon black and lampblack in granular condition.

### Manufacture of Blasting Explosives

The manufacture of the explosive raw materials (nitroglycerin, nitrocellulose, etc.) of dynamites and similar explosives has already been described (see "Noninitiating high explosives"). The operations involved in the production of the finished explosive consist mainly in thoroughly incorporating the components of the explosive mixture, packing them into cartridges of desired size and shape, and packing the cartridges into shipping containers.

The mixing operations involved in the manufacture of commercial explosives are somewhat hazardous; the utmost precautions must be taken to avoid shock, friction, electrostatic sparks, or any other factor that could bring any portion of the explosive mixture to its ignition temperature.

In the manufacture of blasting gelatin, the nitroglycerin and the nitrocellulose are incorporated in specially built mixing machines; the preferred type has two blades which rotate separately to produce thorough incorporation of the components and which are so arranged that the two blades are driven by connected gears, so that they can never strike each other. In some types of mixing machines, the mixing blades hang from vertical shafts, and the bowl, which is movable, is elevated hydraulically at the beginning of the mixing operation until the mixing blades are submerged in the nitroglycerin-nitrocellulose mixture, and is similarly lowered when the mixing operation is complete. Positive stops are provided to prevent the mixing bowl being elevated so far that the revolving blades will make contact with either the bottom or sides of the bowl. In other types of mixing machines, the bowl is fixed in position and the stirring blades are lowered and raised. In still a third type of mixing machine, horizontal mixing arms are employed and the mixing bowl is tilted at the end of the mixing operation to discharge its contents.

The time required to produce complete dispersion of the nitrocellulose in the nitroglycerin may vary from 10 minutes to 1 hour, depending upon the type of mixing machine used. The viscosity of the nitroglycerin is greatly increased in the course of the mixing operation, and the thick viscous mix is extruded in special machines of the sausage-machine type. The design of the extrusion equipment provides special precautions to avoid frictional or other effects that would cause the heating of the mixture. The doughlike mass is usually extruded as a continuous rod of circular cross section, and this rod is cut off in the lengths desired for the final cartridge. These lengths of blasting gelatin may be extruded directly into the cartridge wrapper or may be wrapped in paper. In either case, the ends of the paper cartridge are folded over or crimped,

and the cartridges are packed, usually in 50-lb. boxes. The manufacture of gelatin dynamite and ammonia gelatin dynamite is quite similar to the manufacture of blasting gelatin.

In the manufacture of dynamite, the constituents are mixed very thoroughly in mixers with complete avoidance of rubbing or friction. Since these explosives are not of the firm consistency of blasting gelatin or the gelatin dynamites, the mixing machines do not have to be of such heavy construction. The cartridge wrappers are made separately; the larger sizes are sometimes made by hand and sometimes in automatic machines and the small sizes are almost always made by machine. The packing of the explosive into the cartridges may be done in either of two quite different types of packing machines: one type uses augerlike rotating mandrels to carry the explosive into the paper shell and to pack it to the desired density; and the other uses a reciprocating rammer or tamping member in conjunction with a feeding device. In some packing machines, the cartridges move away from the filling member as they are filled. In most types, however, the rotating mandrel or the reciprocating tamping member rises automatically as each cartridge is filled, and the machine automatically stops the further filling of the cartridges when they have been filled to a designated height. The packing machines, which are of the gang type, load a considerable number of cartridges at one time. After a group of cartridges has been filled, the member that holds the cartridges is moved to another position on the machine, and the filled cartridges are then closed by a device that either automatically folds over the unfilled portion of the shell or crimps it so tightly that the explosive does not work out of the cartridge as a result of any ordinary handling. The resistance of explosive cartridges to water may be increased by making the cartridge wrappers of water-resistant paper, and spraying paraffin upon the finished cartridges or dipping them in molten paraffin maintained at a temperature only slightly above its melting point. Cartridge paper should be strong, water-resistant, and relatively light in weight, since any excess in either the weight of the paper or the amount of paraffin used tends to decrease the oxygen balance of the explosive and to increase the amount of carbon monoxide present in the gases produced by explosion.

### **Economic Aspects of Blasting Explosives**

Statistics concerning the consumption of blasting explosives are of considerable interest since they reflect general industrial activity. This is largely because explosives are essential in the production of such raw materials as coal, iron ore, and limestone.

The U.S. Bureau of Mines compiles statistics of the consumption of industrial explosives in the U.S. Reports for 1947 and 1948 are given in Table XIII. The coal-mining industry is the largest consumer of explosives and, in 1947, consumed 46% of all industrial explosives, bituminous coal mines consuming 36% and anthracite mines 10% of the total 1947 sales. Quarrying and nonmetal mining are the next largest users of explosives, these consuming about half as much explosive as is consumed by the coal-mining industry. Railway and other construction work and metal mining represent other large consumers of explosives. Liquid oxygen explosives were used in 1947 only in bituminous coal strip mines, where their use was almost entirely in the removal of overburden.

TABLE XIII. Consumption of Industrial Explosives in the U.S.

Type of explosive	Apparent consumption, lb.		
	1935-39 (av.)	1947	1948
Black blasting powder:			
Granular.....	31,270,775	9,836,625	8,235,875
Pellet.....	34,080,925	26,627,475	25,003,825
<i>Total black blasting powder.....</i>	<i>65,351,700</i>	<i>36,464,100</i>	<i>33,239,700</i>
High explosives:			
Permissible.....	45,683,634	122,348,571	126,282,153
Other than permissible.....	253,624,298	476,016,727	550,085,616
<i>Total high explosives.....</i>	<i>299,307,932</i>	<i>598,365,298</i>	<i>676,367,769</i>
Liquid oxygen explosives <sup>a</sup> .....	—	16,561,539	15,619,704
<i>Total industrial explosives.....</i>	<i>364,659,632</i>	<i>651,390,937</i>	<i>725,227,173</i>

<sup>a</sup> Data not collected before 1947. The figures given are expressed as the weight of fully saturated cartridges at the time of removal from the soaking box.

Source: *U.S. Bur. Mines, Mineral Market Rept., MMS 1656.*

### Strength of Dynamites

The amount of energy that an explosive produces on explosion or detonation can be determined either by calculation from the known thermochemical factors of the components and the reaction products, or by firing a portion of the explosive in a strong calorimeter bomb especially designed for use with explosives. The energy evolved on the detonation or explosion of four explosives is given in Table XIV. It will be noted that the total energy of 40% straight dynamite is greater than the total energy of 75% guhr dynamite, and its energy is not much less than the total energy of pure nitroglycerin or "100%" blasting gelatin. This is due to the fact that the active dope of 40% dynamite itself produces considerable energy in the reactions that occur when the explosive is detonated, and a similar relationship exists in all of the active-dope dynamites. The manner in which a commercial blasting explosive develops its energy on explosion or detonation is usually a far more important guide to its blasting efficiency in any particular kind of work than is the total energy of the explosive as measured in a calorimetric bomb.

TABLE XIV. Energy Evolved on the Detonation of Various Explosives.

Explosive	Energy from 1 Kg.	
	Kg.-cal.	Kg.-wt.
Nitroglycerin.....	1,567,950	699,292
Blasting gelatin.....	1,537,000	656,081
Dynamite, 40% straight.....	1,255,700	536,006
Dynamite, 75% guhr.....	1,230,000	525,035

Figure 1 (p. 67) shows curves for gelatin dynamite, ammonia gelatin dynamite, straight dynamite, and ammonia dynamite; the approximate rate of detonation is plotted as the vertical axis and the approximate pushing or heaving force is plotted on the horizontal axis in terms of the quantity of TNT that gives an equal swing in the ballistic pendulum. It is important to remember that the curves as shown are only roughly approximate, since different manufacturers often grade their explosives somewhat differently from other manufacturers, in the effort to give the user what each



manufacturer regards as the most satisfactory explosives of that particular rated strength. This variation in the actual characteristics of the explosive, when combined with variations that are inherent in present methods of testing both the rate of detonation and the pushing or heaving force of an explosive as measured by the ballistic pendulum, makes the curves of interest mainly for purposes of broad comparison. The curves show that gelatin dynamites for any given rated strength have higher rates of detonation than ammonia dynamites of the same rated strength, and that the ammonia dynamites for any given rated strength tend to show slightly higher pushing or heaving force than gelatin dynamites of the same rated strength, although the actual differences in some cases are quite small. The straight dynamites are in general intermediate between the gelatin dynamites and the ammonia dynamites, and for any given rated strength show excellent pushing or heaving force.

The ammonium nitrate explosives find their greatest use in blasting work where extremely high brisance or shattering effect is not required and where strong heaving or pushing force is mainly desired; for work of this character they give excellent results.

For work that requires the highest possible shattering effect, well-confined blasting gelatin and the gelatin dynamites usually give excellent results. Confinement is necessary, however, and in the type of shooting known as "mudcapping" (in which a charge of explosive is placed directly against a rock that is to be broken, and the only confinement is that resulting from a layer of clay, mud, or dirt that is placed over the explosive charge), the gelatin dynamites often fail to reach their full rate of detonation or to exert their full explosive force.

For most types of blasting, the highest possible shattering effect is not only unnecessary but may be undesirable, and for work of this character the ammonia gelatin dynamites and the ammonia dynamites are to be preferred to the more brisant gelatin dynamites. For blasting work where maximum gas volume is desirable, ammonium nitrate explosives give excellent results.

## PROPELLANTS

A propellant is specifically defined as an explosive for propelling projectiles (see also *Rocket propellants*). Classified as low explosives, they differ from the detonating high explosives in that the rate of energy release by autocombustion can be controlled within limitations. Without this element of control, some propellants, such as smokeless powder, may be caused to undergo detonation and so act as a high explosive. This is because the most important ingredients of smokeless powder, such as nitrocellulose and nitroglycerin, are detonating high explosives. Thus, the control feature governs the classification of the material.

### Ballistic Properties of Propellants

In firing a propellant powder in a cannon, careful consideration must be given to the rate of energy release as well as to the total energy released by the powder. These considerations are usually referred to as interior ballistics. Numerous methods of calculation are used to formulate and design powders to meet certain specific ballistic performance requirements, most of which are based on empirical formulas that are not adequate to include wide variations, particularly in powder compositions. There are, however, certain basic concepts that are included in all calculation methods.

The potential thermal energy of a propellant powder, when fired in a cannon, is

converted into the kinetic energy of the projectile. The total energy that can be communicated to the projectile is limited by the length of travel of the projectile in the gun tube, and the pressure that the gun tube can withstand, regardless of the energy of the powder. Figure 2 represents a typical pressure-travel curve for a projectile in a cannon. The maximum allowable pressure is determined by the strength of the gun. The maximum pressure is reached at point A, with respect to the distance the projectile has traveled from its starting point. Thus, in an already existing weapon, the powder must transmit its energy to the projectile at a rate indicated by this curve in order to attain the maximum efficiency from the powder. If, on the other hand, the powder is already fixed, the weapon must be designed to withstand the indicated pressures throughout this curve. If the weapon will not do this, rupture will undoubtedly occur. The projectile energy is represented by the area under this curve and may be expressed as:  $W = \int P dV = \frac{1}{2}mv^2$ , where  $W$  is equal to the work performed;  $P$  the

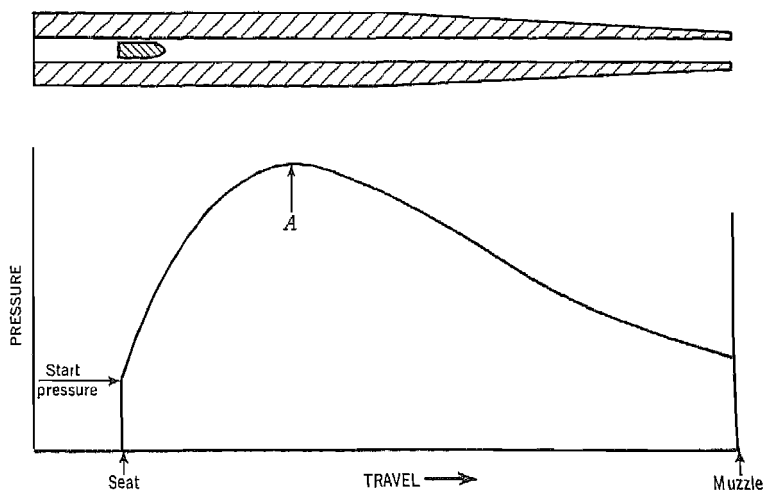


Fig. 2. Typical pressure-travel curve for a projectile in a cannon.

pressure;  $V$  the volume;  $m$  the mass of the projectile; and  $v$  the muzzle velocity. If a curve is drawn representing the pressure that the weapon can withstand along the bore of the gun, it will be found to be somewhat above the powder curve, to an extent dependent upon the gun designer's choice of a safety factor.

Providing the propellant selected for use has sufficient energy, the problem of designing it to meet the pressure-travel requirements as closely as possible is primarily one of adjusting the geometrical design of the grain to meet the desired rate of pressure build-up; this is based upon the rate of burning of the powder and upon the surface exposed for burning and its relation to the travel of the projectile.

Since the burning of powder occurs only on the surface, if the composition is fixed, the rate of burning under constant-pressure conditions for a grain of powder is dependent upon the surface, and the time of burning is dependent upon the thickness of powder that must be burned. In powder design, this thickness is designated as the "web." In flake granulations such as are used in sporting powder, the web is considered to be the length of the grain. In single-perforated powders it is established as the thickness of the tube wall.

There are three modes of burning to be considered. These are designated as de-

gressive, neutral, and progressive. These may be represented by the curves in Figure 3. In a solid grain (cord), the surface decreases continually and the burning is degressive. If the grain is perforated, the interior surface increases while the exterior surface decreases, and neutral or even progressive burning can be obtained.

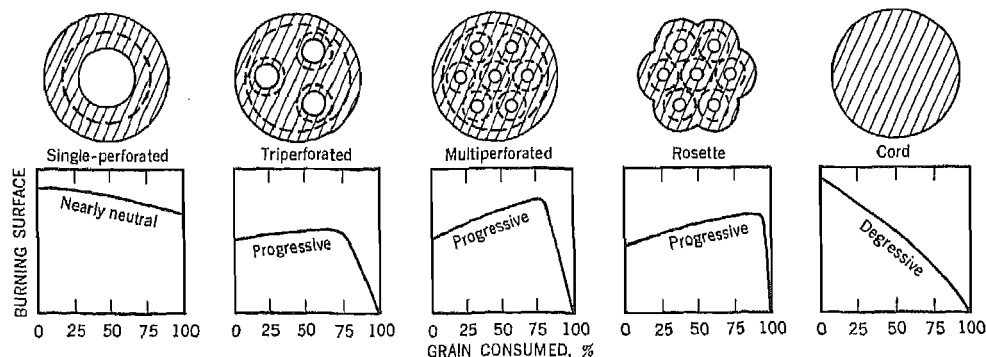


Fig. 3. Modes of burning of perforated grains and cord. (The dotted lines represent approximately the position at which the inward burning and the outward burning first meet.)

The action in weapons of the three modes of burning is shown by the curves in Figure 4. If the areas under the three curves are equal, the muzzle velocity of the projectile, other things being equal, will be the same for all types of granulation, the differences being only in the rate of release of energy and the maximum pressure attained.

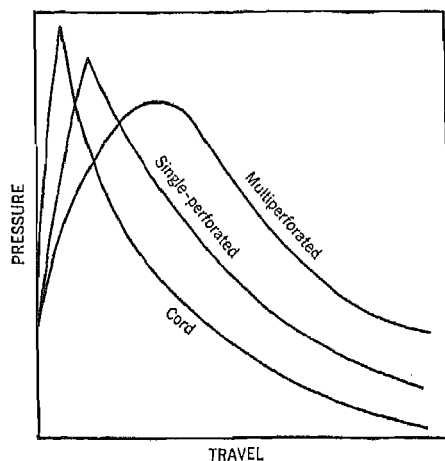


Fig. 4. Pressure-travel curves for various grains.

When it becomes necessary to establish the optimum web for a new powder composition in a weapon, it is essential that it be done by actual firing tests, since there are no known methods of calculation that can be employed with certainty. In general, it is found that the pressure will vary inversely as the web of the powder; that is, as the web is made smaller the pressure obtained from a given weight of charge becomes greater. Both the pressure in the tube and the velocity of the projectile obtained with a given powder increase directly with the weight of powder used until a critical point is reached where the pressure will rise very sharply without a corresponding increase in velocity; in order to pre-

vent the erratic performance of the powder in a weapon, the web must be so adjusted as to give the desired velocity at pressures well below the point of "pressure break." Once the relationship between web, weight of charge, pressure, and velocity has been established for a powder composition in a specific weapon, reasonably accurate predictions can be made as to the performance of a particular lot of powder by the determination of its thermal properties in closed bomb tests,

### Black Powder

The first real propellant was black powder made from potassium nitrate, sulfur, and charcoal. Until the end of the 16th century, it was used in the form of a fine powder or dust, whence its name. Owing to the difficulty experienced in loading from the muzzle with the powder in this form, it was found expedient to granulate the powder into small agglomerations, thus permitting it to flow more readily, and to some degree to control its rate of burning. The first marked improvement in performance characteristics of black powder occurred in 1860 when General Rodman of the U.S. Army discovered the principle that the rate of release of energy could be controlled by the form and density of the powder grain. To obtain this control, the finely divided powder was pressed into larger grains with definite geometrical form. By providing a grain with a hole through the center, General Rodman was able to counteract the degressive burning of a solid grain. This advance in the art of powder design was of considerable importance since it permitted the use of lightweight weapons owing to the ability of the powder designer to provide powders that give low pressures over long periods of time rather than high pressures for short periods. Although black powder remained the only practicable propellant for several hundred years, its use left much to be desired, since in weapons of that day it caused considerable fouling of the piece, which was accompanied by undue corrosion. This necessitated frequent cleaning and complete replacement of the weapon. Black powder is extremely hygroscopic and requires more than usual care in handling to keep it dry and usable. For military purposes, it possessed the decided disadvantage of producing vast quantities of smoke and, in some instances, brilliant flashes; thus it revealed the location of the emplacements to the enemy. In the dry state, black powder is sensitive to friction and to heat; thus, it presents an additional problem in handling, which under stress of battle conditions has resulted in serious consequences.

### Smokeless Powders

There was, as a result of the deficiencies in black powder, a continued emphasis placed on the development of improved powders. About 1838, Pelouze observed the action of nitric acid upon cellulose, and thus was produced the first nitrocellulose, the basis of all modern gunpowders (see p. 35; see also Vol. 3, p. 361).

In 1846, Schönbein, a Swiss scientist, evolved methods of manufacturing nitrocellulose in which he succeeded in interesting several European governments. In the course of development, disastrous explosions occurred in several plants, since the chemical properties of nitrocellulose were little understood. The first successful substitution for black powder was made by one Major Schultze, a Prussian Army officer. In general, Schultze's powders consisted of nitrocellulose in admixture with an oxidant such as sodium or potassium nitrate. For the most part they were too fast-burning and not entirely suitable for rifled weapons. In 1884, a French engineer, Paul Vieille, discovered that nitrocellulose incorporated with a mixture of ether-alcohol could be kneaded much the same as bread dough to produce a colloided mass, which in turn could be rolled out into thin sheets, cut into small squares, and dried. This was the first smokeless powder and was called "Powder B" in honor of General Boulanger. During the years 1888 and 1889, nitrocellulose was combined with nitroglycerin by Nobel to form a smokeless powder of the Ballistite and Cordite types.

Today, every nation employs modern smokeless powders consisting principally

of colloidized nitrocellulose, either as such or in admixture with nitroglycerin or other materials, both for sporting and military purposes. These powders, when ignited, burn only on the surface, and the rate of energy release can be accurately controlled so that one formulation can meet the performance requirements over a wide range of weapons by merely changing the geometric form and size of grain. These products, although called smokeless powders, are in reality not powders in the accepted sense of the word, nor are they smokeless, except in comparison with black powder.

Modern powders are manufactured in many forms, which include flakes, strips, pellets, and cylinders. The cylindrical grain form is most commonly employed for military purposes by the U.S., although strips, flakes, and strands are used by many European countries. Flake and pelleted forms are most commonly used in the sporting-type ammunition (see Fig. 5).

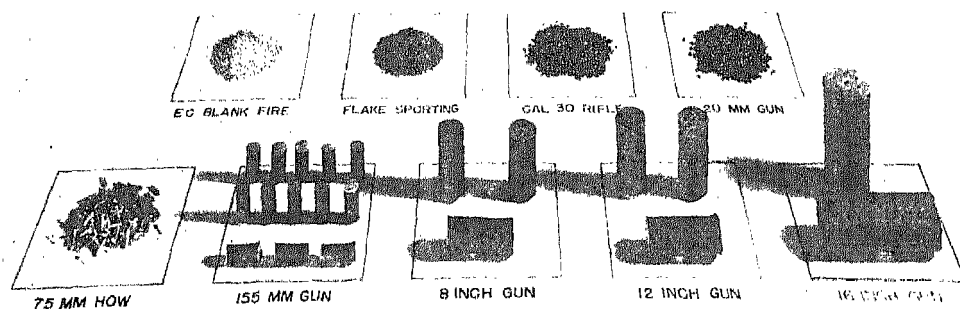


Fig. 5. Forms of smokeless powders. (The largest grain shown is 2 in.  $\times$   $\frac{3}{4}$  in.)

In general, smokeless powders may be classified with regard to formula as shown in Table XV (p. 83).

#### PARTIALLY COLLOIDED SINGLE-BASE POWDERS

These partially colloidized propellants are frequently referred to as Schultze powder (after the originator) or E.C. powder (Explosives Company, an English company, one of the early manufacturers). More generally they are referred to as bulk powders, probably because they were loaded in bulk, volume for volume with black powder. This type of powder is extremely fast-burning because of the uncolloidized nitrocellulose, and, for the same reason, is more sensitive to friction than are the more common colloidized types of powder. Owing to the presence of the potassium and barium nitrates as well as the uncolloidized nitrocellulose in the formula, such powders are particularly hygroscopic and care must be taken to prevent their exposure to moisture. They are commonly used in commercial shotgun ammunition, blank ammunition, and for military purposes in fragmentation hand grenades. Certain manufacturers add to the formulation small amounts of dye, which serves only as an identifier. The powder has a rough surface because it consists of agglomerates of nitrocellulose fibers in admixture with the other constituents (see Table XVA).

In the U.S., these powders are manufactured by either one of two processes. In the earlier process, the materials are incorporated, in the presence of water, by mechanical means, such as those employed in the manufacture of black powder, which

results in fairly uniform distribution of the several ingredients. The mass is then rubbed through a perforated plate to give it more or less granular form. It is then tumbled in a "sweetie barrel," which rotates in a bath of hot water, and thus the granules are transformed into roughly spherical shapes and at the same time the water is removed. This produces loosely agglomerated granules, which will not stick to the walls of the "sweetie barrel." These granules are screened through a 12-mesh sieve and the coarse material is returned to the wheel mill to be reworked. The powder that passes the sieve is further dried to harden the grains. After this treatment, the powder is placed in a horizontal tumbling barrel and a solvent for the nitrocellulose is added. This solvent is usually a mixture of acetone and alcohol or benzene, although other solvents may be employed. This solvent mixture has a softening and swelling action upon the nitrocellulose fibers and causes them to stick together. As the tumbling barrel is rotated, heat is applied by circulating a stream of hot air through the tumbling powder; this removes the solvent, leaving surface-hardened spherical grains consisting of partially colloided nitrocellulose in admixture with the other powder constituents. These hardened grains are screened through appropriate sieves to give a uniform granulation of the pellets within the sieve limits. The powder is then given a final drying treatment and packed in moisture-tight containers. The moisture content of the finished powder is generally under 2%. Some care must be exercised in the choice of type and quantity of solvent used in this process because, if the solvent action of the mixture is too great, or if too much is employed, a solid mass of powder will result; and, if the solvent action of the mixture is insufficient, the resulting powder will be too friable to handle in any future loading operation.

The second procedure, more recently developed, provides for mixing the nitrocellulose, by slurry methods, in water in which the soluble constituents are dissolved. This operation is accomplished in a closed vessel called a still. After mixing is completed, a water-immiscible solvent such as a mixture of butyl acetate and benzene, in which the water-insoluble ingredients such as diphenylamine have been dissolved, is added to the slurry. The resulting mixture is agitated with considerable violence; this causes the solvent phase to be dispersed in the water phase in the form of small droplets around which the nitrocellulose fiber builds up. The agitation is continued, and the solvent is distilled under vacuum in such a manner that the water distillate is returned to the still. When the solvent has been completely removed, the partially colloided powder granules and a water solution of the soluble salts remain in the still. The solids are removed by filtration and dried, the desired amount of salts being left in the dried powder.

The granulation of the powder is determined by the manufacturing procedure and by screening to produce the desired uniformity. The actual granulation may vary considerably, depending upon the end use of the powder. For example, a powder for blank cartridges may consist of granules all of which pass through a No. 10 U.S. sieve and 97% of which pass through a No. 12 U.S. sieve and are retained on a No. 50 U.S. sieve. The same powder, when used in hand grenades, may merely be required to pass through a No. 6 U.S. sieve. The granulation of the powder, all other things being equal, is the control of the powder "quickness" or rate of charge burning. The term "quickness" should not be confused with the term "rate of burning" of the composition, which is independent of the granulation. The quickness for a given composition is dependent upon the surface available for burning and, therefore, upon granulation.

The constituents of this type of powder can vary considerably without seriously affecting the performance of the powder. The major constituents are permitted in military specifications to vary by  $\pm 2\%$ . The methods of chemical analysis are for the most part standard. On the other hand, functioning tests, which are determined from the end use of the powder, vary considerably. U.S. Army Specification No. 50-13-8B for E.C. powder prescribed two functioning tests. One, a fragmentation test, requires that a hand grenade loaded with a specified weight of powder shall be fragmented to give  $40 \pm 10$  fragments large enough to be held on a 2-mesh screen. The second test, employed when the powder is to be used in blank ammunition, requires that in not more than 1% of the tests made, the wad from the round loaded with a specified weight of powder when fired in a caliber .30 rifle shall not penetrate a kraft screen placed at a specified distance in front of the muzzle of the rifle.

#### COLLOIDED SINGLE-BASE POWDERS

The term "single-base powders" does not accurately define all powders falling in this class. Its generally accepted definition includes all powders containing as their principal constituent nitrocellulose in a colloid state without the presence of nitroglycerin. The discovery of Paul Vieille that nitrocellulose could be colloidized or dispersed in suitable solvents and then extruded or otherwise formed into pellets, strips, or grains with predetermined surfaces is the basis for the design and manufacture of all modern powders. The first smokeless powder of this type consisted only of colloidized nitrocellulose, but since that time efforts have been continually under way to modify this original powder to give improved performance either as regards ballistic performance or chemical and physical properties. Typical examples of single-base powder formulations are shown in Table XVB.

In the U.S., single-base colloidized powders generally are used for military purposes, although they are sometimes employed as propellants for sporting ammunition.

The methods used in their manufacture have been generally standardized and vary only in minor detail. The steps in their manufacture are as follows: (1) dehydration of nitrocellulose; (2) colloidizing; (3) graining; (4) drying; (5) blending.

Complete and detailed descriptions of these steps are to be found in numerous texts on the subject of explosives and powders. The first operation in actual powder-manufacturing procedure consists of the dehydration of the nitrocellulose. Owing to the extreme sensitivity of dry nitrocellulose and the hazard attendant in handling such a material, it is transported and received at the plant wetted so as to contain approximately 30% of water. This water must be removed before the colloidizing operation, since the presence of even a small percentage of water makes difficult, if not impossible, the subsequent colloidizing operation. This operation was originally accomplished by the obvious process of drying the nitrocellulose. This procedure, however, was found to be extremely hazardous and resulted in frequent disastrous explosions in plants, both in this country and abroad. The process, now referred to as dehydration, which was developed largely to reduce the hazard of manufacture, has been so successful that now explosions occur only rarely. The process provides for the replacement of the water in the fibrous nitrocellulose with ethyl alcohol. This procedure is carried out batchwise, with batches of from 25 to 50 lb. of nitrocellulose. The charge is placed in a hydraulic press, and most of the water in the nitrocellulose is squeezed out by applying pressure of approximately 250 p.s.i. to the charge. The pressure is released and a definite weight of alcohol is pumped through

the loosely consolidated charge. Pressure is then reapplied up to 3500 p.s.i. for a definite period of time, after which it is released and the block of "alcohol-wet" nitrocellulose is removed from the press. The process is so controlled as to leave in the block a definite weight of alcohol, which becomes a part of the solvent in the subsequent colloid operations.

In general, alcohol will not act as a solvent for nitrocellulose when the nitrogen content of the nitrocellulose is above 12.2%. If the nitrogen content is less than this value, difficulty will be encountered since partial solution may occur in the process. This difficulty is overcome by either increasing the water content of the alcohol, which reduces its solvent power, or reducing the pressure and time of "dwell." A number of serious fires and detonations have occurred in this process throughout the years, and, in most instances, they may be attributed to the too rapid application of pressure after the addition of the alcohol to the charge. This may result in the entrapment of air and alcohol to form pockets within the charge, which ignite under pressure and, in turn, cause the ignition or detonation of the nitrocellulose.

In the next operation, a predetermined quantity of the dehydrated nitrocellulose is placed in a dough-type mixer, the solvent and other ingredients are added, and the preliminary colloid operation is started. Most modern single-base powders are colloid by the addition of a mixed solvent consisting of 2 parts of ether to 1 part of alcohol, neither of which has any appreciable colloid or solvent effect upon nitrocellulose when used alone. In admixture, however, they will completely disperse nitrocellulose having a nitrogen content up to 12.6%. As the nitrogen content of the nitrocellulose is increased, the solvent power is reduced until, at 13.4% nitrogen, little or no solution occurs. When a powder formulation calls for nitrocellulose having a nitrogen content greater than 12.6%, it is usually obtained by blending proper proportions of pyrocellulose (12.6% nitrogen) and guncotton (13.4% nitrogen), which assures the presence of soluble material at all times. If this is not done, other more powerful solvents must be employed to secure the proper degree of gelatinization. The quantity of solvent used will vary, of course, with the formulation and other conditions of manufacture; however, it will, in general, be employed up to approximately 1 part of solvent to 1 part of dry ingredients. This mixing operation continues for about 1 hour and does not completely disperse or colloid the powder mixture, although it would do so if the mixing time were prolonged for a sufficient period. When the mass is removed from the mixer, it is in a partially colloid state and has the appearance of dry oatmeal. To speed up the colloid action, the mixture is subjected to a preliminary "blocking" treatment, which involves pressing the mass for several minutes at a pressure of approximately 3000 p.s.i. This treatment further colloids the powder and converts it into a solid block. This block is transferred to a second press in which it is forced through a series of screens and perforated plates, an operation that further colloids the mass. This procedure is referred to as "macaroni" pressing, since the powder as it comes from the press has much the appearance of that product. The shredded or "macaronied" powder is then reblocked, after which it is uniformly colloid and is ready for graining. During these steps in the colloid procedure, the highly volatile solvents used are rapidly leaving the powder mass and care must be taken to transport the powder from one operation to the next in closed containers to minimize this solvent loss. Modern plants are equipped with vapor-removal systems that recover a large part of this solvent.

The blocks are next transferred to the graining press, which forces the mass



through dies of predetermined dimensions and shapes to give a granulation, when dried, having the required dimensions to meet the particular ballistic performance requirement. The dimensions of these dies are governed first by the dimensions of the desired finished grain, but they must be designed to allow for the shrinkage of the powder that occurs in the drying or solvent-removal operation. This shrinkage will vary considerably with composition and grain dimensions. An average value for shrinkage across the grain is about 25% while lengthwise the shrinkage will amount to approximately 10%.

The powder comes from the graining press in long continuous strands, often perforated, which must then be cut into appropriate lengths. This is accomplished by passing the strands past a moving or rotating blade or series of blades, the speed of the blades and feed of the powder governing the length of cut.

The next step in the process provides for the removal of the solvent from the powder. This is usually referred to as "solvent recovery" although the recovery is only incidental to the actual requirement for a dry or essentially solvent-free powder. The procedure requires careful control because, if the solvent is removed too rapidly from the grains, a surface or skin hardening occurs that prolongs the removal time and may prevent the complete removal of the solvent. The mass of powder is placed in large tanks and warm air is passed through it. The solvent-laden vapors are passed over cooling coils and their solvent content reduced to the desired degree, after which they are recirculated over heating coils and sent back through the powder mass; thus, the solvent is removed continuously. By controlling the temperature of the heating and cooling coils as well as the flow of air, the solvent-removal rate can be controlled. The temperature is raised gradually over the drying period but is not permitted to exceed 65° C. The time of drying varies considerably (2-14 days) and is dependent upon the size of granulation and composition of the powder. To remove all of the solvent from the powder in this manner would require excessively long treatment; therefore, when the solvent content is reduced to approximately 6%, it is removed from the recovery tanks and placed in large vats of warm water, and the solvent content is further reduced. When this solvent-removal treatment is complete, the residual solvent remaining in the powder will vary from 0.3 to 5%, depending largely upon the size of the powder granule. After it is removed from the water-drying vats, the powder is air-dried to remove the surface moisture and screened to remove dust and grain clusters.

Since conditions of manufacture vary from day to day, and because performance requirements for the powder are very exacting, particularly when it is to be used for military purposes, it is necessary to blend the powder to minimize the unavoidable manufacturing variations. This "blending" is accomplished by transferring the powder by gravity fall from one bin to another. Blending is in some instances accomplished by tumbling the powder in barrels until a uniform product is obtained. This operation assures a thorough mixing or blending of large quantities of powder. The blended lots for large-caliber weapons usually amount to 100,000 lb. For small-arms and sporting powders the lots are smaller, running from 15,000 to 50,000 lb. Powders are not blended to combine two or more compositions or granulations except in rare instances, and then only to meet some special requirement.

Where extremely long grains of powder are involved, as is the case in many European countries, this blending operation is either omitted entirely or the powder is hand-blended by cross blending the powder from many boxes.

When powders are to be volumetrically loaded, as is the case with most sporting and small-arms powders, they are coated with a thin layer of graphite to permit the powder to flow freely through the loading machines. The use of graphite as a coating on the powder grains also reduces the tendency of the powder to develop on its surface a static charge of electricity, thereby rendering the powder somewhat safer to handle. Following the blending operation, the powder is packed in airtight containers in which long periods of safe storage may be expected.

The earlier single-base powders of the type shown in Table XVB in column 1 (pyro powder) had certain disadvantages and, almost since their inception, efforts have been underway by all major governments and commercial powder companies to minimize these deficiencies. The principal disadvantageous characteristic is the tendency of the powder to absorb moisture. The amount of water absorbed by pyro

TABLE XV. Nominal Compositions of Smokeless Powders.

Constituent	1	2	3	4	5
A. Partially colloid single-base powders					
Nitrocellulose, %.....	80.00	80.00	87.00	84.00	
Nitrogen, %.....	13.20	12.90	12.90	13.15	
Barium nitrate, %.....	8.00	6.00	6.00	7.50	
Potassium nitrate, %.....	8.00	3.00	2.00	7.50	
Starch, %.....	2.75	1.00	—	—	
Paraffin oil, %.....	—	—	4.00	—	
Diphenylamine, %.....	0.75	1.00	1.00	1.00	
Dye (Aurine), %.....	0.25	—	—	—	
B. Colloid single-base powders					
Nitrocellulose, %.....	99.00	97.70	90.00	85.00	79.00
Nitrogen, %.....	12.60	13.15	13.15	13.15	12.60
Dinitrotoluene, %.....	—	—	8.00	10.00	—
TNT, %.....	—	—	—	—	15.00
Di- <i>n</i> -butyl phthalate, %.....	—	—	2.00	5.00	—
Triacetin, %.....	—	—	—	—	5.00
Tin, %.....	—	0.75	—	—	—
Graphite, %.....	—	—	—	—	0.20 <sup>a</sup>
Diphenylamine, %.....	1.00	0.80	1.00 <sup>a</sup>	1.00 <sup>a</sup>	1.00
Potassium sulfate, %.....	—	0.75	—	—	—
C. Double-base powders <sup>b</sup>					
Nitrocellulose, %.....	77.45	52.15	51.50	50.50	
Nitrogen, %.....	13.15	13.25	13.25	12.20	
Nitroglycerin, %.....	19.50	43.00	43.00	28.00	
Diethyl phthalate, %.....	—	3.00	3.25	—	
Potassium sulfate, %.....	—	1.25	1.25	1.50 <sup>a</sup>	
Potassium nitrate, %.....	0.75	—	—	—	
Barium nitrate, %.....	1.40	—	—	—	
Carbon black, %.....	—	—	0.20 <sup>a</sup>	—	
Candelilla wax, %.....	—	—	0.08 <sup>a</sup>	0.08 <sup>a</sup>	
Methyl cellulose, %.....	—	—	0.10 <sup>a</sup>	0.50 <sup>a</sup>	
Dinitrotoluene, %.....	—	—	—	11.00	
Ethyl centralite, %.....	0.60	0.60	1.00	4.50	
Graphite, %.....	0.30	—	—	—	

<sup>a</sup> These constituents are added to the basic composition.

<sup>b</sup> Type 1 is the solvent type; types 2, 3, and 4 are the nonsolvent type.

powder will vary somewhat with the web but, in general, will not exceed 3% based on the dry weight of the powder.

This degree of hygroscopicity in the powder is sufficient to result in a marked change in its ballistic performance with changing atmospheric conditions. A second and important deficiency from a military standpoint is the fact that brilliant muzzle flashes are obtained when rounds containing this powder are fired; and these reveal to enemy troops the location of the gun emplacements. Developments following World War I resulted in the manufacture of powders having markedly improved properties as regards both hygroscopicity and flashing characteristics. Typical of these developments are those compositions indicated in columns 4 and 5 in Table XVb. These powders are frequently referred to as flashless nonhygroscopic powders (FNH). The nonhygroscopic property, which is only a relative term since even these powders absorb up to 1% moisture, was obtained by the addition to the basic nitrocellulose of sufficient quantities of nonvolatile waterproofing plasticizer, such as dibutyl phthalate or triacetin, to effect some degree of moistureproofing. The quantity of this type of inert material was limited, since it reduced materially the ballistic potential of the powder. In some instances, this was overcome by a change in type of nitrocellulose to one with a higher degree of nitration. The flash from the powder is known to be due, in general, to the fact that the high temperature of the burnt powder gases as they emerge from the muzzle of a gun causes reaction of these with the oxygen of the air. Thus, if the burnt gas temperature could be reduced sufficiently, flash would be eliminated. Since further addition of inert materials to the formula would result in too great a reduction in potential of the powder, powder manufacturers resorted to using material such as dinitrotoluene, which has low ballistic potential. By these changes in formulation, powders of reduced hygroscopicity, which were flashless in certain weapons but not in all, were obtained. While these improvements were obtained, they were accompanied by two major disadvantages. The first of these was the low potential of the compositions, which made necessary the use of greater quantities of powder; in some instances sufficient powder could not be loaded in already existing cartridge cases. The second disadvantage was that the inert, and in most instances carbonaceous, material produced a considerable amount of smoke, which in daytime firings was almost as objectionable as the flash that it replaced. A second method of reducing or eliminating the flash from weapons where high potential is required is by the addition of small percentages of the salts of the alkali metals. The action of these salts in reducing flash is not definitely known; and, though they are extremely effective flash reducers, their presence in powder compositions is invariably accompanied by a considerable amount of smoke.

#### DOUBLE-BASE POWDERS

The term "double-base," however nondescriptive, has been applied to powders containing nitrocellulose and nitroglycerin as the principal constituents. These powders are used both for military and sporting purposes, and may contain from 15 to 40% nitroglycerin. They are made by two general methods. The first is somewhat similar to that employed in the manufacture of single-base colloidized powders, except that the solvent used is alcohol-acetone instead of ether-alcohol, and the solvent-recovery procedure is omitted. The latter omission is made because of the hazard involved in recovering nitroglycerin-bearing solvents. Therefore, although the powder is dried, the solvent is not recovered. The second method is referred to as the

nonsolvent method and is used only where the quantities of nitroglycerin and other colloidizing agents are approximately 40% or greater. In this process, the usual dehydration process is omitted and the colloidizing is effected by passing the water-wet nitrocellulose, in admixture with nitroglycerin and the other powder constituents, between heated rolls. This operation squeezes out a large part of the water and permits the nitroglycerin to partially colloid the nitrocellulose. Repeated passes through the rolls remove the remaining moisture and produce a sheet of thoroughly colloidized powder. If the powder is to be used in sheet form, as it is in trench mortars, the thickness of the sheet must be very closely controlled, and varies from 0.004 to 0.0125 in., depending upon the weapon for which it is being made. If, on the other hand, it is to be later extruded in the form of large grains used principally for rocket work, the sheet may be as thick as 0.125 in. and special care regarding thickness is not required. Table XVC shows a few of the double-base powder compositions commonly employed in modern weapons and rockets.

In general, double-base powders are of greater ballistic potential than single-base powders, and are quite nonhygroscopic. They are said by some manufacturers to give more uniform performance than single-base powders. If this is so, it is very likely due to the greater degree of colloidizing that is obtained with the higher percentages of plasticizers, including nitroglycerin, used in these powders. The double-base powders are difficult to render flashless because of their high burning temperature. Their use as rocket powders is almost mandatory because of their energy and burning-rate characteristics and the fact that large-size grains can be made without the use of a volatile solvent. The removal of volatile solvent from large grains would be extremely slow, if at all practicable, since such grains may be as much as 20 in. in diameter.

In spite of these desirable performance features of double-base powders, they have many undesirable characteristics. For example, they have a high burning temperature, which causes excessive barrel erosion when compared with single-base powders. Also, the material nitroglycerin is hazardous to handle, and many disastrous explosions have occurred in the manufacture of this type of powder. For military purposes, the use of double-base powders has been limited owing to the critical nature of glycerin, the supply of which has been, until recently, limited to that produced by the soap and fat-rendering industries. This limitation has now been largely removed with the advent of the synthetic production of glycerin, which utilizes petroleum as a raw material.

#### BALL POWDER

In 1933, a commercial group in the U.S. developed a new type of powder, involving an entirely different manufacturing procedure than had been used in the past for the manufacture of solvent types of powder. This powder is granulated in the form of small spheres of controlled size to meet the ballistic requirements of the weapon for which the powder is designed. The ingredients commonly used in this type of powder do not differ markedly from those used in other solvent-type powders, and the manufacture of both single- and double-base powders is practicable. The use of these powders in the U.S. has been confined to military small-arms ammunition, small-caliber cannon, and sporting ammunition.

The manufacture of ball powder, as it is called, starts with nitrocellulose in a water slurry. This slurry is charged into a still where the nitrocellulose is dissolved in a solvent such as ethyl acetate. To this solution is added a stabilizer, diphenyl-

amine, and neutralizer, such as chalk, the latter being added to neutralize such acid as may be present in the nitrocellulose and released upon its solution in the ethyl acetate. If a double-base powder is to be made, the required quantity of nitroglycerin is now added to the mixture. Upon agitation, the lacquer solution is dispersed in the form of small globules, which are more or less fixed in size by the addition of a protective colloid and the speed of agitation.

When the desired degree of dispersion has been obtained, the solvent is driven off by the application of heat to the still charge; the solvent is recovered and re-used; and solidified powder is separated from the water and screened to give pellets of the desired size. The powder then is coated with a deterrent such as dinitrotoluene or ethyl centralite (*N,N'*-diethylcarbanilide) to effect the desired mode of burning, after which it is dried to remove the water and packed for shipment. The oversized ball powder may be passed through rolls to reduce its web thickness to the desired degree. The powder may be graphitized, as in other small granulations of powder, to increase its density of loading, to induce free flow, and to reduce the accumulation of a static charge on the powder.

The process is said by its originators to produce a more stable powder than can be produced by more conventional powder-manufacturing methods, when the purity of the basic ingredients used in the respective processes is the same. It is probably true that basic materials of lower purity can be employed in the ball powder process to give a finished product of equal stability to that obtained by the more commonly used manufacturing methods.

Since the process is accomplished entirely under water, except in the final drying stage, less hazard in production is undoubtedly involved; and less capital cost of production facilities, as well as less time for processing, probably attend the new process. Because the process is accomplished under water, water-soluble salts or other water-soluble ingredients cannot be readily incorporated in the powder. A complete description of the process will be found in the December 1946 issue of *Chemical Engineering*.

#### STABILITY OF SMOKELESS POWDER

The term "stability" as applied to smokeless powder refers to the resistance of the powder to chemical deterioration. The term is, however, occasionally used when referring to the ballistic stability of a powder. In the preparation of nitrocellulose, the principal ingredient in most smokeless powder, great care is exerted to produce a highly purified product that has a high degree of chemical stability. Similar precautions are taken in prescribing the purity of other powder constituents. In spite of these precautions, it is found necessary to add stabilizing chemicals to all modern powder compositions to insure an acceptable stability life of the finished powder. The two principal stabilizers employed are diphenylamine and ethyl centralite.

The nitrocellulose used in the manufacture of smokeless powder is said to be stable or to have good stability when it passes the potassium iodide test and the heat test at 134.5°C. The stability of finished military powders is determined by the heat test at 134.5°C. and a surveillance test at 65.5°C. For double-base powders, a heat test at 120°C. is used instead of the higher 134.5°C. heat test. It may be stated, however, that there is no test for the stability of smokeless powder that is infallible, or that may be used in more than a general way to evaluate either the life of the powder or its safety as regards storage.

All organic compounds can be decomposed by heat and all explosive mixtures have the common property of undergoing decomposition when subjected to only moderately elevated temperatures. Nitrocellulose and nitroglycerin, the principal constituents of smokeless powder, are less resistant to heat than are most other explosives. Therefore the stability of the powder reflects largely the stability of one or both of these materials. Smokeless powder will decompose so rapidly at temperatures above 200°C. that spontaneous combustion will occur within a few minutes. The rate of decomposition decreases sharply with a decrease in temperature, until at normal atmospheric temperatures only slight decomposition will occur over a period of many years. Smokeless powder will also decompose, although slowly, if moisture is present. This decomposition is further promoted if either acid or alkali is present. For many years, powder manufacturers used a dye in their powders to act as an indicator in the presence of acid, which was formed by the decomposition of nitrocellulose. Thus, when the color of the powder changed owing to a change of dye color in the presence of acid, the powder was discarded as unstable. The dye most commonly used was Rosaniline. It was later discovered that a stabilizing effect could be obtained by the use in powder formulas of the chemical diphenylamine. This chemical does not prevent decomposition, but prevents acceleration of the rate of decomposition by combining with the nitrogen oxides liberated by the decomposition of nitrocellulose. By such combination, stable compounds such as *N*-nitrosodiphenylamine, dinitrodiphenylamine, and trinitrodiphenylamine are formed. To illustrate the values obtained for certain powders in regard to stability, the data in Table XVI are presented for several of the powder types previously referred to (Table XV).

TABLE XVI. Stability Values for Smokeless Powders.

Powder compn. as in Table XV	134.5°C. Heat test		120°C. Heat test		65°C. Surveillance test, days
	S.P. <sup>a</sup>	R.F. <sup>b</sup>	S.P. <sup>a</sup>	R.F. <sup>b</sup>	
B1.....	90	150	—	—	600
B4.....	50	80	—	—	1500
B5.....	65	130	—	—	900
C1.....	—	—	85	165	300
C4.....	—	—	95	275	1300+

<sup>a</sup> S.P. = time, in minutes, to turn methyl violet paper to a salmon-pink color.

<sup>b</sup> R.F. = time, in minutes, for red fumes to develop.

As with all explosive materials, smokeless powder should be stored in clean dry magazines that are maintained at fairly low temperatures. Particular care should be exerted to keep the powder from being contaminated with foreign substances.

In general, smokeless powder will not detonate from shock, except in cases of powders containing high percentages of nitroglycerin or powders of very fine granulation.

When smokeless powder is stored in considerable depth, detonation may result from very rapid rise in temperature due to fire. In general, the finer granulations of the powder will be more likely to detonate than will the coarser granulations.

## TESTING OF EXPLOSIVES

The most important tests used to establish the suitability of explosives for commercial or military use, or for comparison of explosives, are those that determine the

sensitivity, stability, brisance, and power. If an explosive is found to be satisfactory in these respects, additional tests for hygroscopicity, volatility, solubility, density, compatibility with other materials, and resistance to hydrolysis are necessary before a final evaluation can be made. Propellants are tested especially for stability, since sensitivity is of secondary importance and ballistic potential is determined by functioning tests in weapons. Brief descriptions of the tests for explosive and stability characteristics are given here.

#### SENSITIVITY

**Impact Tests.** Sensitivity to impact is determined by subjecting a small quantity of confined explosive to the transmitted shock from a falling weight—usually 2 kg.—and determining the minimum height of fall that will cause at least one explosion in ten tests. With the Bureau of Mines apparatus (Test B), 0.02 gram of materka is spread evenly over an area 1 cm. in diameter and confined by means of a 2-g.1 plunger having a tip 1 cm. in diameter. The falling weight strikes the upper end of the plunger. If the explosive is liquid, the sample is held in position by being absorbed in a disk of dried filter paper 1 cm. in diameter. With the Picatinny Arsenal apparatus (Test A), the cavity in a steel cup is filled with the solid or liquid explosive, the cup is covered with a cylindrical brass cover having a slip fit, and a small steel plug is placed on the center of the brass cover. In this test, the falling weight strikes the steel plug.

**Explosion Temperature Tests.** Sensitivity to explosion by heat is determined as the temperature required to cause explosion either in 5 seconds or in less than 0.1 second. In the first case, a sample of 0.02 gram is placed in a gilding-metal blasting-cap shell, and the lower end of this shell is plunged into a bath of molten Wood's metal at a measured temperature. The time required to cause explosion, flashing, or very rapid decomposition is noted with a stop watch. The temperature for explosion in 5 seconds can be obtained by making a number of tests at various temperatures and plotting a temperature-time of explosion curve. The temperature required for instantaneous (less than 0.1 second) explosion is determined by dropping small crystals of the explosive on the surface of molten metal held at a measured temperature. The time required for explosion is noted, and the temperature is varied until the minimum temperature required for instantaneous explosion, flashing, or decomposition is obtained. Not all explosives undergo detonation in explosion temperature tests; in some cases, decomposition is accompanied by a puff of gas and smoke, and, in other cases, there is no violent evolution of gas or smoke.

**Pendulum Friction Test.** Sensitivity to friction is determined by this test. A 7-gram sample of the explosive is spread evenly over a scored steel base plate, and a 20-kg. steel shoe falling from a height of 1.5 m. is allowed to sweep back and forth pendulumwise across the base plate. The rod carrying the shoe must have been adjusted so that the shoe will slide across the plate  $18 \pm 1$  times when no explosive is present. Tests of ten samples are made and the number of snaps, cracklings, ignitions, and/or explosions is noted.

**Rifle Bullet Impact Test.** A bomb is prepared by screwing a closing cap to one end of a 2-in.-long piece of cast-iron pipe that is 2 in. in diameter and threaded at both ends. The bomb is filled with the liquid, pressed, or cast explosive and is closed by screwing on a closing cup. With the loaded bomb in a vertical position, a caliber .30 bullet is fired through it from a distance of 30 ft. At least five such tests are made and the number of explosions is noted.

**Sensitivity to Initiation.** This is determined by a modification of the sand test. A 0.40-gram sample of the explosive is pressed into an empty blasting cap, and successive charges of 0.10 gram Tetryl and 0.20 gram lead azide are pressed on top of this. Five such assemblies are fired in the sand test bomb, and the average amount of sand crushed, after correction for that crushed by the Tetryl and azide, is determined. In succeeding tests, the minimum amount of Tetryl or of lead azide alone required to cause crushing of the same amount of sand is determined.

#### BRISANCE

**Sand Test.** Brisance or shattering power can be determined by the sand test. A 0.40-gram sample of the explosive is pressed into a metal blasting cap under a pressure of 3000 p.s.i. Charges of 0.10 gram Tetryl and 0.20 gram lead azide are added under the same pressure, and, finally, a reinforcing cap is pressed against the top charge. An 8-in. length of miner's fuse is inserted in the cap and crimped tightly in place. The detonator so assembled is centered in a bomb containing 80 grams Ottawa sand of such fineness that all passes through a No. 20 sieve but none passes through a No. 30 sieve. Then, 120 grams more of Ottawa sand is added, the bomb is closed, and the charge is fired by igniting the fuse protruding through a hole in the top plate. The amount of sand crushed is determined by weighing the portion passing through a No. 30 sieve. This is corrected by subtracting the separately determined weight of sand crushed by 0.10 gram Tetryl and 0.20 gram lead azide. The net weight so obtained is representative of the 0.40-gram charge of explosive under test. Flame-sensitive initiating explosives such as lead azide or mercury fulminate, of course, require no superimposed charges for this test.

#### POWER

**Ballistic Pendulum Test.** This test utilizes the equality of action and reaction to measure explosive power. A sample of the explosive is detonated in a heavy mortar suspended by a pendulum bar and closed by means of a loosely fitting steel cylinder weighing 36 lb. An adjacent scale is provided to show the angular deflection of the mortar from its position of rest when the steel plug is ejected in the opposite direction. In practice, the deflection caused by 10 grams TNT is determined, and the weight of other explosive required to produce approximately the same deflection is determined. The weight required to produce exactly the same deflection is calculated. From this and the 10 grams TNT, the relative power of the other explosive is calculated.

**Trauzl Lead Block Test.** This test is made by exploding a 10-gram charge of the explosive in a cylindrical cavity, 25 mm. in diameter and 125 mm. deep, in a cylindrical lead block, 200 mm. in height and diameter. The sample is wrapped in tin foil, with a detonator embedded in the charge, and is placed at the bottom of the cavity. The cavity is stemmed with sand. After the charge is fired, the volume of the cavity is determined by pouring in water from a graduate. The enlargement caused by the explosive sample is found by subtracting from the determined volume, the original volume plus the enlargement caused by the detonator. The enlargement caused by the detonator is determined separately in the same manner.

**Heat of Explosion.** The work capacity or power of an explosive or propellant can be determined by measuring the heat liberated during detonation or autocombustion in an inert atmosphere. With high explosives, this is done in a very large calorimetric bomb, which permits explosives to be detonated without rupture of the bomb



Propellants can be tested in much smaller calorimetric bombs, in which samples of only 1–2 grams are ignited by means of an electrically heated wire.

#### STABILITY

**65.5°C. Surveillance Test.** This test is applied chiefly to propellants, but it can be applied to explosives. A 45-gram sample is placed in a flint-glass bottle having a ground-glass stopper. The bottle is placed in an oven or chamber maintained at  $65.5 \pm 1.0^\circ \text{C}$ . Visual observation is made daily for the appearance of red fumes, which is considered the end of the test. The number of days required to cause the liberation of red fumes is taken to represent the relative stability of the propellant or explosive, and tests of 30 days or less are considered to indicate hazardous instability. Deterioration can be established by periodic tests of the propellant.

**75°C. International Test.** A 10-gram sample of the explosive is transferred to a tared weighing bottle, 35 mm. in diameter and 50 mm. deep. A watchglass is placed over the top of the bottle so that it is loosely covered. The bottle and contents are heated at  $75^\circ \text{C}$ . for 48 hours, cooled, weighed, and examined for fumes or decomposition, as indicated by appearance or odor. If the loss in weight exceeds the moisture content of the sample, volatility or decomposition is indicated.

**100°C. Heat Test.** The moisture content of the explosive to be tested is determined by drying a weighed 10-gram portion in a desiccator until constant weight is attained, and calculating the loss in weight as percentage of moisture. Weighed 0.60-gram portions of the sample are transferred to each of two test tubes, 75 mm. in length and 10 mm. in diameter, one of which has been tared. The tubes and contents are placed in an oven maintained at  $100 \pm 1^\circ \text{C}$ . At the end of 48 hours, the tared tube is removed, cooled, weighed, and replaced in the oven. After an additional 48 hours of heating, the tube and contents are again cooled and weighed. The percentage of loss during each heating period is calculated, correcting for the moisture present as previously determined. The untared tube and contents are heated at  $100^\circ \text{C}$ . for 100 hours, and any ignition or explosion is noted.

**Vacuum Stability Tests.** A weighed 5-gram sample of the explosive is transferred to a glass heating tube so designed that the ground neck can be sealed with mercury after a calibrated capillary tube with a ground stopper end has been connected to the heating tube. The capillary tube is of  $\wedge$  shape and the lower end consists of a cup. About 7 ml. of mercury is placed in the cup, and the system is evacuated until the pressure is reduced to approximately 5 mm. The level to which the mercury has risen in the capillary tube is recorded, and the heating tube is inserted in a constant-temperature bath maintained at 100, 120, or  $150^\circ \text{C}$ . If an excessive amount (11+ ml.) of gas is not liberated, heating is continued for 40 hours. After the apparatus has cooled, the level to which the mercury in the capillary tube has fallen is noted. From the difference between the initial and final levels and the volume of the capillary per unit of length, the volume of gas liberated during heating is calculated. If the explosive is highly sensitive or very powerful, a 1-gram sample is used in making this test.

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**EXT D&C DYES.** See *Azo dyes*, Vol. 2, p. 266; *Colors for foods, drugs, and cosmetics*.

## EXTRACTION

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### LIQUID-SOLID EXTRACTION

The extraction of solids by solvents, or liquid-solid extraction, is a unit operation in which components are separated from solids by dissolving them in liquids. This operation is expressed in the different industries by various words, such as washing, leaching, lixiviation, elution, elutriation, diffusion, percolation, decoction, decantation, infusion, maceration, digestion, steeping, and dissolution, all referring to the transfer of soluble materials from solids to water or other solvents.

The soluble material, often called the solute, may be a solid or a liquid dispersed through the insoluble solids, coating their surfaces, dissolved in a liquid adhering to or entrained in the solids, or, in many cases of animal or vegetable matter, located within their cellular structure. The solids usually undergo mechanical and often thermal treatment before extraction to make the solute accessible to solvent action through one

or more material-preparation or conditioning operations, such as crushing, roasting, rolling, grinding, pressing, flaking, heating, steaming, or moistening.

Extraction operations are used extensively throughout the chemical and allied industries and have actual or potential applications wherever impure solids are processed. See "Manufacture" under *Alkaloids*; *Caffeine*; *Fats and fatty oils*; and many other articles. See also *Solvents*.

The most widespread use of this unit operation is in the manufacture of pharmaceuticals where practically all products of animal or plant origin undergo one or more solvent extractions in their recovery and purification. Extractions with water, with dilute and concentrated alcohols, and with acetone are common. These solvents are often modified, as by the addition of acids, alkalies, or salts, to make the extractions either more thorough or more selective. Water-immiscible hydrocarbons are also frequently used. Crushed or ground plant materials, so extracted, serve as a source of alkaloids, glucosides, vitamins, and other drugs. The operation is also important in the production of many types of antibiotics. Animal tissues are the source of various hormones, primarily obtained by solvent extraction. Insecticides can also be recovered from plant materials by solvent methods.

Perfumes, spice oils, flavoring extracts, and essential oils can be obtained from natural sources, primarily through some sort of solvent-extraction process. Soluble coffee is obtained from its bean and soluble tea from its leaf by hot-water extraction, and the caffeine can be removed and recovered from such materials by use of the proper solvents. The recoveries of edible vegetable oils from nuts, beans, and seeds, and of industrial fats and oils are accomplished to an appreciable and increasing extent by solvent extraction on a large-tonnage scale. Waxes are obtained from plant materials, many previously considered waste, by use of the proper solvents. Solvent extraction has been applied on a commercial basis to the removal and recovery of oils and fats from raw wool, garbage, and a number of packing-house by-products. Glues and gelatin are produced from animal materials by heating and extracting with water.

Plant proteins used for adhesives, water paints, paper sizing, plastics, and coatings are recovered and concentrated by solvent extraction from vegetable materials, often from meals that had been subjected to a prior extraction of oils. Tannins and natural dyestuffs are extracted, in many cases with water, from bark, wood, and other plant materials. Rosins, turpentine, and terpene derivatives are also recovered from materials such as pine-tree stumps by use of hydrocarbon solvents. The water washing of paper pulp to remove sulfate and sulfite liquors can be properly considered and treated as a solvent-extraction operation, as can the dry cleaning of clothing, and metal degreasing.

### Methods of Extraction

Regardless of the materials considered, the prepared solids can be handled by *single-batch* extraction, in which case the total solids charge is placed in a single vessel for solvent application; or the extraction may be accomplished by *multibatch* methods, in which several separate charges in different stages of extraction are treated by a cyclic, sequence flow of solvent quantities. The *continuous* method for extraction also may be used, in which case the solids are introduced, subjected to solvent treatment, and then are discharged from the extraction system in a more or less uninterrupted, steady flow.

Each of these methods of solids handling may be further classified by the manner in which the solvent is applied to the solids. For such purposes, the general terms *spray percolation*, *full immersion*, and *intermittent drainage* may be used. These methods are illustrated in Figure 1 as applied to a simplified form of single-batch extraction. Multibatch and continuous applications will be given later.

In each case is shown a vessel with a false bottom that holds a charge of solids. In spray percolation, the solvent is sprayed onto the top of the charge, trickles without flooding through the interstices of the solids, drips through the false bottom, and collects for discharge. In full immersion, inflowing solvent completely immerses or floods the solids for the duration of the extraction. One batch of solvent may remain in the vessel for the extraction, or a constant or periodic throughflow of solvent, entering either from top or bottom, may be maintained for a more thorough extraction of solute from the solids charge.

Intermittent drainage is a means of extraction in which the solids are covered with the liquid and then drained before submerging with more liquid. This solvent application followed by drainage is carried out two or more times.

#### BATCH EXTRACTION

Commercial extractions on numerous solid materials are frequently done by single-batch methods and equipment using simple false-bottom vats, such as are shown sche-

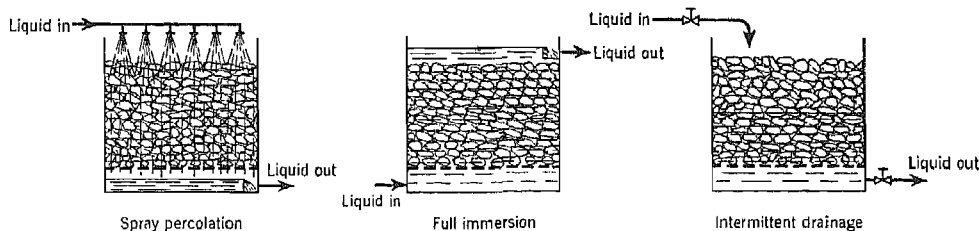


Fig. 1. Methods for extraction of solids with solvents.

matically in Figure 1. The vessels may be cylindrical, conical, or of rectangular cross section, and are usually inexpensively constructed of metal, concrete, or wood. Solid charges may be from a few pounds to several tons and are often loaded and discharged manually. The vessels may have means for agitation, such as mechanical stirrers, or steam or air jets. They sometimes are jacketed for steam heating or are fitted with heating coils beneath the false bottom. They can be fully enclosed and are often designed for pressure. The false bottoms can support a fine-mesh screen or may be covered with filtering material. Mechanical means are applied, in many cases, for filling the vessel with solids or for discharging. In some modifications, the equipment is designed to suspend by vigorous agitation finely divided solids in the solvent; if the solids are not heavy enough to settle out readily after extraction, they must be removed by filtration. Another method for extracting finely divided material is to deposit it as a cake on the filtering cloth of filter equipment, and then wash the cake with solvent to remove the entrained or occluded materials. Because of the short contact time, appreciable quantities of solvent are required and the operation is inefficient.

However, in the simplest methods for single-batch extraction, no vessels are used.

These are the place-leaching and heap-leaching methods used for extracting huge quantities of materials, where extractions are slow, or handling charges and equipment costs would, by other methods, be excessive for the value of the products recovered. In place leaching, the solid material is left in its natural location and flooded with water. In heap leaching, the material is arranged in piles near the place where it is obtained or previously processed and then treated with water. The methods have been used for the recovery of copper from low-grade ore, treating low-quality caliche for sodium nitrate, and the extraction of certain salts from their material sources (5).

**Batch Equipment.** A well-established form of batch-extraction equipment consists of a jacketed cylindrical vessel with dished heads, and fitted with a solids agitator.

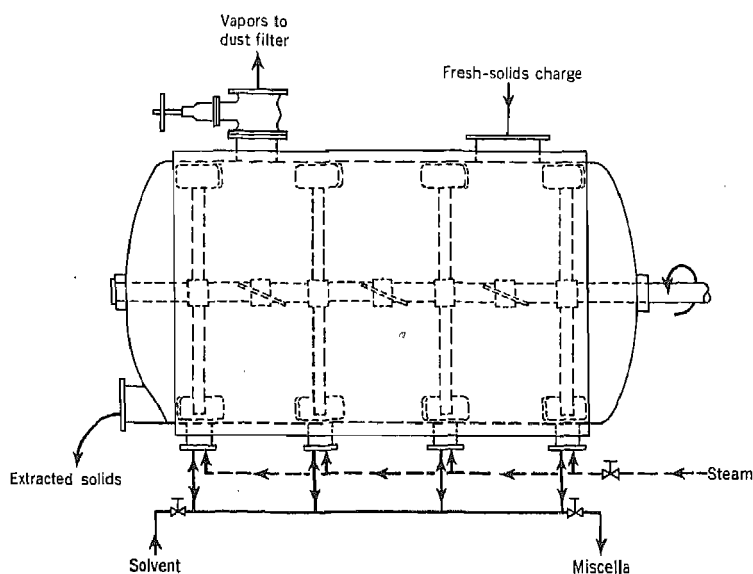


Fig. 2. Horizontal-type steam-jacketed batch extractor with agitators.

A typical design, used in the recovery of tallows and greases from packing-house materials, is shown diagrammatically in Figure 2. A vessel of this type, about 6 ft. in diameter by 9 ft. long, will hold approximately  $3\frac{1}{2}$  tons of meat cracklings. The solvents normally used are petroleum fractions, approximating heptane or hexane, or the chlorinated hydrocarbons.

In the intermittent drainage method the cracklings charge is subjected to three or more solvent treatments. The extractor is filled each time with fresh solvent, introduced at the bottom through screen-covered nozzles, while the charge is agitated. The solvent containing the dissolved tallow is then drained through the same nozzles without agitation. After the final extraction and drainage, the solvent retained in the solids charge is vaporized by heating through the jacket and steam-sparging through the bottom nozzles. The vapors leave through a top vapor nozzle, pass through a dust filter, and then flow to the condensers for solvent recovery. The thoroughly steamed, vapor-free charge is then moved out of the extractor through the discharge door by means of the agitator. In some operations, solvent-tallow solutions, stored from an

intermediate or final treatment of a previous charge, are used as the first or early liquid application to a charge to obtain higher tallow concentrations.

Horizontal rotary extractors are also used for batch extraction. The vessels turn on trunnions, thus agitating the solid charges. A procedure similar to the stationary batch-extraction operation is used, that is, charging, intermittent drainage, steaming, and discharging. Among the known applications of such equipment are the alcohol extractions of grains and other vegetable materials for the removal of oils and waxes, from which vitamins and other pharmaceuticals are subsequently recovered; the extraction of oil from castor pomace with a heptane solvent; and the recovery of caffeine from tea wastes.

#### MULTIBATCH EXTRACTION

In multibatch extraction, a group or battery of batch-extraction vessels is used. These vessels may be of any of the types and modifications described in single-batch extraction, or of special design for battery operation. Each in turn is charged with the

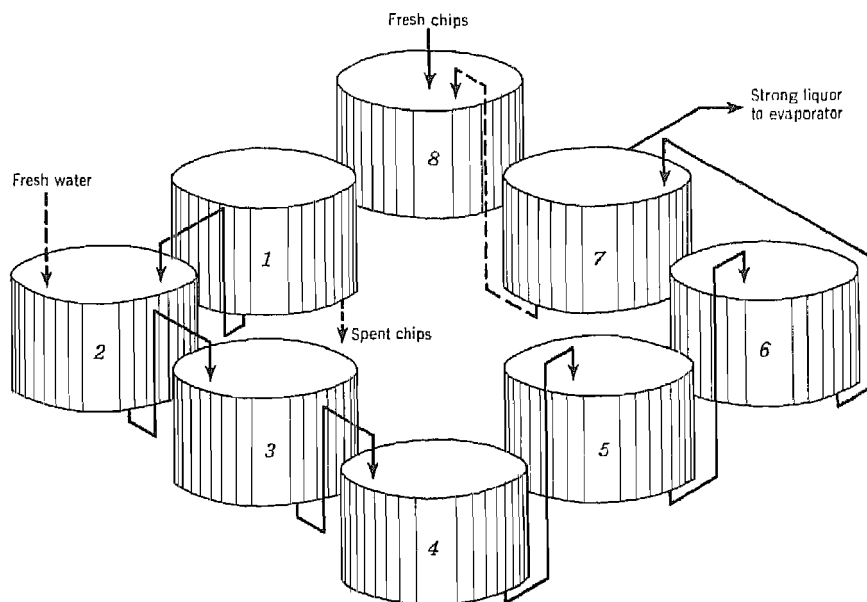


Fig. 3. Battery of extractor tubs in multibatch countercurrent operation.

solids. Usually, the solvent quantities flow through each of the vessels in a given order to treat progressively the less exhausted solids charges, and then leave the system as strong extract liquids after passing through a freshly filled charge. The most extracted charge, after being treated with fresh solvent just entering the battery, is drained of liquid and cut out of the system for discharge of solids and refill of a fresh charge.

**Extraction Batteries.** This multibatch operation is more clearly illustrated by Figure 3, showing diagrammatically a leach system such as is used for obtaining tannin extract from wood or bark. This specific tannin leach system consists of a battery of 8 tubs, although as many as 24 tubs can be used. These tubs are cylindrical in shape,

usually about 14–16 ft. in diameter and 12–16 ft. deep. They are filled with wood chips and are extracted by hot water pumped through the tubs in sequence. The fresh incoming water is applied to the most nearly exhausted chips, and the strong extract solution is applied to the fresh chips before it leaves the system.

As an example of such an operation, while tub 8 in Figure 3 is being filled with fresh chips, strong extract liquor is drawn off from tub 7, and liquor is moved forward in sequence from preceding tubs until tub 1 is drained. Next, while discharging spent chips from tub 1, tub 8 is filled with liquid from the preceding tub, the liquid again is moved forward in sequence, and tub 2 is filled with fresh water. This process is then repeated after advancing one tub, that is, tub 1 is filled with fresh chips while drawing off liquor from tub 8 and emptying tub 2 of liquor through sequence flow; and so the multibatch extraction continues. The complete cycle from the time a given tub is filled with fresh chips until its spent chips are discharged may be 24 hours or more.

A number of variations of a leaching cycle are in use. In many, more than one tub is cut out of the solvent flow system at a given time to allow a longer period for loading and discharging the vessels. A comprehensive study of variations in multibatch extraction cycles that relates by formulas and examples the number of cells and number of solvent treatments for each charge is given later in this discussion (see p. 104).

The operation can be carried out by the full immersion method, known in the tannin industry as "diffusion." Here, the chips are always covered with liquid throughout the extraction, the outflow from one tub displacing the liquid from the next tub. Alternatively, the intermittent drainage method, known in the tannin industry as "decoction," may be used: liquid is fully drained from a given tub before it is filled by draining a preceding tub in the transfer sequence. In some cases even spray percolation is used: the liquid pumped from the bottom of one tub is sprayed onto the chips in the next tub and allowed to drain through that charge of chips.

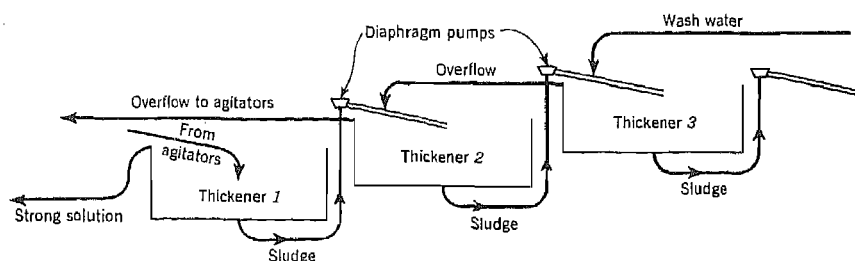
For tannin materials that can tolerate higher temperatures, batteries of autoclaves or enclosed pressure vessels can be used. These vessels are 15–25 ft. high and 5–8 ft. in diameter. They are made of copper, stainless steel, or iron lined with brick. A similar cyclic operation, as described for the open tubs, is employed, using either full immersion or intermittent drainage methods. The autoclaves are usually operated at about 50 p.s.i. pressure and 250°F. Extraction can be performed in far less time than is possible by the use of open leach tubs.

In the sugar industry, diffusion batteries are used to water-extract the sugar-beet slices. The battery is made up of closed pressure vessels operating by the full immersion method in a multibatch sequence-flow cycle. This is similar to the method employed for tannin extraction batteries. Each vessel is preceded by a heat exchanger for heating the liquid.

#### CONTINUOUS EXTRACTION

Many types of continuous equipment have been devised for solvent extraction, a number of these in Europe for the diffusion of beet sugar, a hot-water-extraction operation (5). In all such equipment, a prime consideration is a mechanical means for conveying the solids at a uniform rate through the system, either as a smooth, steady stream or in sizable increments or quantities carried through at close intervals. Solvent normally flows through the solids in a truly countercurrent direction to the solids movement, although there are some exceptions.

A frequently presented example of continuous countercurrent extraction is the operation of a series of Dorr thickeners. Each thickener is a shallow, cylindrical tank of large diameter, normally used to separate liquid from solids by settling. The mixture of liquid and solids enters the tank through a central feed well in the top, and as it moves radially outward, the solids settle on the bottom as a thick slurry which is continuously moved by scraper blades to the center for discharge through the tank bottom. The clear liquid overflows the edges of the tank into a peripheral trough. By operation of a number of these thickeners in series so that the solid slurries flow from tank to tank in a direction opposite to the flow of the clarified liquids, continuous countercurrent extraction is obtained as shown in Figure 4. This method is often referred to as continuous countercurrent decantation. Dorr-thickener units have been applied commercially to the washing of finely divided solids, such as crystals, chemical precipitates, and ground ores, free from liquids containing dissolved matter. See *Sedimentation*.



*Courtesy The Dorr Company.*

Fig. 4. Continuous countercurrent decantation (10).

There are several large-tonnage industries in the U.S. where continuous extraction could be effectively applied, as in sugar-beet diffusion, tannin leaching, and animal-fat recovery. However, the development and use of continuous extraction with non-aqueous solvents has been slow in the U.S., except in the vegetable-oil industry for the recovery of edible and industrial oils. It is through this last-named industry that continuous nonaqueous solvent extraction has become firmly established in the U.S.

There are five main types of continuous extractors used in the U.S. for vegetable-oil extraction. Two of these types are improved modifications of the most popular European designs; the other three types are considered primarily American developments. The solvent used in vegetable-oil extraction is usually a petroleum fraction, approximating hexane, although chlorinated hydrocarbons, particularly trichloroethylene, have been applied in some cases. There has been some interest in the use of alcohols as solvents.

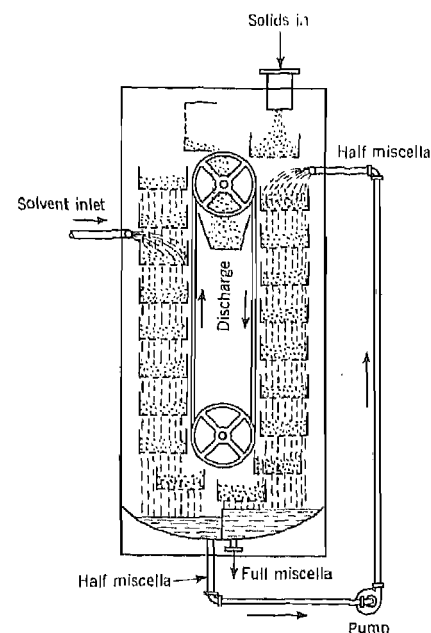
Most of the installations are for extracting flaked soybeans, which can be easily handled in these machines. The residual oils in press cake from hydraulic pressing or expeller operations can also be readily recovered by the various types of continuous extractors. Difficulties in extracting some of the higher-oil-content vegetable materials are being overcome. Progress has also been made in the solvent extraction of marine oils and animal fats.

**Continuous Equipment.** In considering the main types of continuous extraction equipment for vegetable-oil extraction, classification in accordance with the method of applying solvent can be used.



The spray percolation method is represented by the Bollmann-type continuous extractor (see Fig. 5) of German origin, but adopted and modified by American equipment manufacturers. This extractor consists of a continuous series of suspended baskets with perforated bottoms. As these baskets revolve within the housing, they are automatically filled in turn with the prepared oil-seed and, after completing an extraction cycle, are automatically discharged. Fresh solvent is continuously sprayed onto each basket containing the most extracted material as it moves upward, before draining and discharge. This solvent then drips in turn through the upward-moving baskets in countercurrent flow, and collects at the bottom of the extractor. This liquor, known as half miscella, is then pumped to spray onto the freshly charged top basket of the downward-moving side of the revolving series of baskets. It trickles through these baskets in cocurrent flow to collect as full-strength miscella at the bottom.

Fig. 5. Bollmann-type continuous extractor.



The full immersion method is represented by three main types of extractors. The Hil-

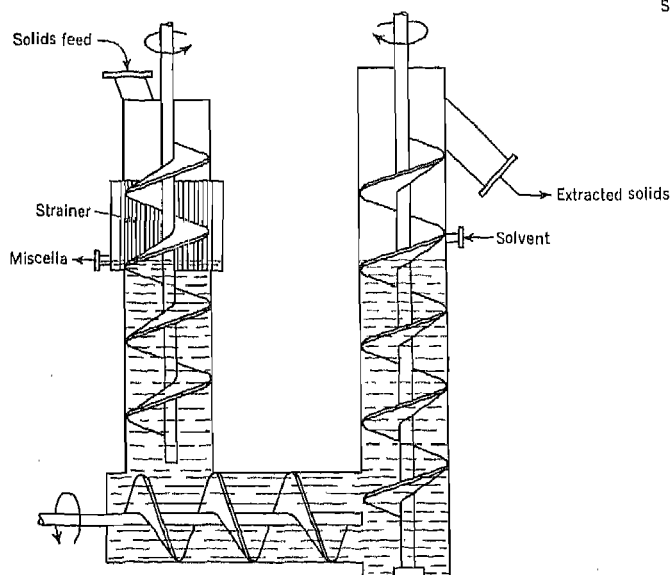


Fig. 6. Hildebrandt-type extractor.

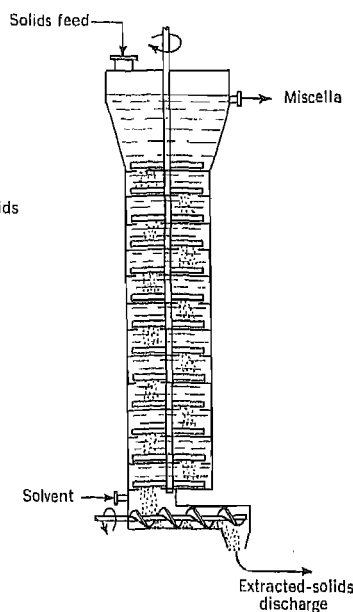


Fig. 7. Bonotto-type extractor.

debrandt type, also of German origin, is illustrated in Figure 6. It consists of a series of three sections of screw conveyors in a cylindrical housing to form a U. The slowly revolving screw conveyors carry the solids from the top of one vertical sec-

tion down and around to the top of the other vertical section. This is in counterflow to the solvent which floods all but the upper spaces of the extractor.

The Bonotto-type extractor (see Fig. 7) also operates flooded with solvent, which flows upward. In a vertical column, equally spaced plates loaded with solids revolve under stationary scraper blades, or in other designs, the plates are stationary and the scraper blades revolve with the central shaft. The solids enter at the top,

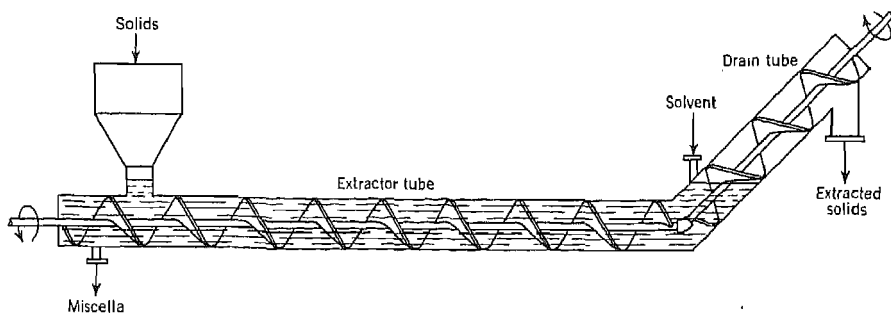
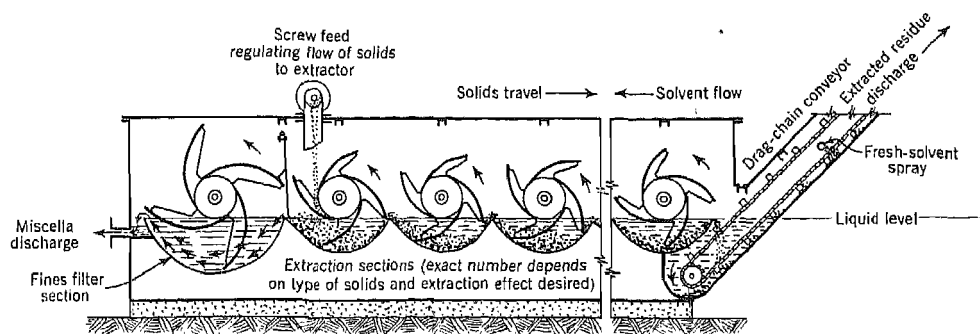


Fig. 8. Screw-conveyor-type extractor.

and fall by gravity from plate to plate down the column, being carried to the open sections in the plates by revolving movements of plates or scrapers. This type and modifications of it are built by several manufacturers.

The third full immersion extractor design consists primarily of a horizontal or inclined screw conveyor in a cylindrical steel housing. The solvent fills the extraction section of the housing and moves in counterflow to the solids carried through by the



*Courtesy Vulcan Copper & Supply Co*

Fig. 9. Kennedy continuous countercurrent extractor.

screw conveyor. Equipment of this class generally uses petroleum fractions as solvents, but one of this type uses only chlorinated hydrocarbon solvents (see Fig. 8).

Intermittent drainage extraction is also represented in the vegetable-oil industry (see Fig. 9). In this unit, the solids are moved from compartment to compartment by slowly revolving impeller blades in counterflow to solvent. Intermittent drainage is accomplished when the impeller blades lift the solids above the liquid level before the

solids fall over to the next compartment. A fresh solvent wash and final drainage is accomplished on the extracted material as it is carried up by the horizontal flights of the drag-chain conveyor.

### **Theory of Solvent Extraction of Solids**

In determining the physical principles that control the transfer of a liquid or solid solute from the inert solids, with which it is associated, to the surrounding liquid medium, in which it dissolves, consideration must be given to the various ways in which the solute may be held by the solids.

As previously indicated, the solute may be in solution adhering to the surfaces of the solids or retained in the interstices between the solids. It may, as undissolved material, coat the surfaces of the solids or fill crevices or pores in the surfaces. It can be deposited in the porous structure or capillaries that riddle certain types of solids. As other possibilities, the solute can be dispersed through the solids, enclosed in cells, or adsorbed at various depths into the solid fragments.

The one or more ways by which the solute is physically combined with the solids depends on the source or nature of the materials and their mechanical or chemical treatment before or in preparation for solvent extraction. The manner in which the solute is distributed in the solids is the determining factor as to accessibility of the solvent to the solute for extraction, the ease by which solute transfer takes place, and the physical laws governing such transfer. Only in comparatively few practical cases has the structure of the solids and solute distribution been sufficiently understood to serve as a basis for a valid analysis of solute-transfer principles.

### **Method of Material Balances**

The usual approach to setting up design equations and to solving extraction problems involves the use of a number of material balances. It is normally used for and most effectively applied to the intermittent drainage types of extraction. Material balances are made for both solute and solvent quantities in the extracting liquid and entrained in the solids. Overall balances are made to cover the terminal conditions, and stepwise material balances are obtained for the beginning, ending, and intermediate stages.

#### **SINGLE-BATCH EXTRACTION**

As an illustration consider the treatment of a batch of solids by the intermittent drainage method of Figure 1. For mathematical purposes, designate the solute and solution weights associated with a solids charge by lower case letters  $s$  and  $w$ , respectively, and the quantities of the solute and solution of the extracting liquor fed to or drained from the charge by the capital letters  $S$  and  $W$ . Appropriate subscript symbols are used with these letters to designate the specific quantities.

As shown in Figure 10, for the first extraction treatment the original solids charge contains a weight quantity of solute,  $s_0$ , and a weight of solute plus entrained solvent expressed by  $w_0$ . A weight of solution  $W_F$  containing  $S_F$  weight units of solute flows onto the charge. After a given time for contacting and extraction, the solution  $W_1$  containing  $S_1$  solute is drained from the solids charge, leaving in the solids the quantity  $s_1$  of solute and a total weight of solute plus solvent equal to  $w_1$ .

Simple weight balances for the first treatment are:

$$S_F + s_0 = S_1 + s_1 \quad (1)$$

$$W_F + w_0 = W_1 + w_1 \quad (2)$$

Generally,  $S_F$ ,  $s_0$ ,  $W_F$ , and  $w_0$  are known. Therefore, one of the other quantities at the right of each equation must be set or determined for solving the equations. If one cannot resort to adequate measurements of these quantities in actual operation, then  $s_1$  and  $w_1$  are determined by relating them to the other quantities.

In equation (1), the value of the solute quantity left in the solids after the extraction is influenced by the distribution and location of the original solute in the solids and by this solute's accessibility to solvent action. Thus,  $s_1$  is definitely determined by the physical factors of the solids charge. Also affecting this solute quantity is the time of solute exposure to the solvent and the degree of approach to equilibrium solute-transfer conditions between the liquid entrained in the solids and the surrounding liquid. In general, for a given preparation of the solids material,  $s_1$  would be a function of the concentration  $S_1/W_1$  of the solution drawn off from the charge, with a correction factor for that quantity of solute, contained in the solids, not available for dissolving.

In equation (2),  $w_1$  is the quantity determined, assumed, or otherwise obtained as a fixed value, or it may be related to variables of the operation such as density, viscosity, and surface tension. For a given form, structure, state of subdivision, and type of solids, and a fixed method of packing them in the extraction vessel,  $w_1$  will probably be a function of the concentration  $S_1/W_1$  of the liquid withdrawn. With  $s_1$  and  $w_1$  determined by such relationships,  $S_1$  and  $W_1$  could then be calculated.

The solids charge remaining after this first treatment with liquid can then be treated with another quantity of solution, as in the second extraction treatment shown in Figure 10, and equations similar to (1) and (2) can be set up as follows:

$$S_G + s_1 = S_2 + s_2 \quad (3)$$

$$W_G + w_1 = W_2 + w_2 \quad (4)$$

With the inflowing liquid quantities,  $S_G$  and  $W_G$ , known and  $s_1$  and  $w_1$  obtained in the analysis of equations (1) and (2), the right-hand quantities of equations (3) and (4) can be determined by procedures similar to those for the first treatment. In this manner, equations can be set up and solved for each of the succeeding treatments with liquid to determine, after any number of treatments, the extent of removal of solute from the solids charge and the amounts and concentrations of the extract liquids withdrawn.

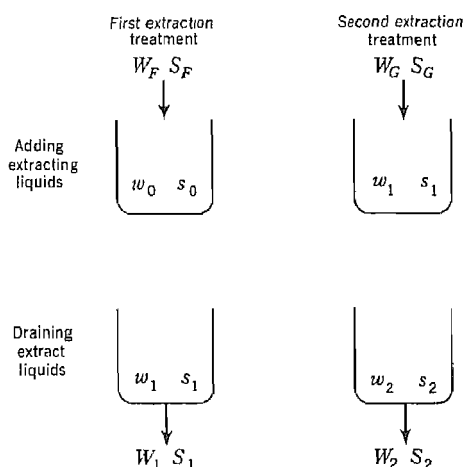


Fig. 10. Single-batch extraction.

Since, as discussed later, relationships between the solvent and solute quantities in the solids and the surrounding liquids have not been sufficiently developed theoretically for general applications, experimental or operating data and simplifying assumptions are normally required in solving extraction problems.

**Equilibrium Conditions.** To permit ready mathematical calculations, certain ideal conditions, approached in many actual extractions, are set up. First, the solids are assumed to be nonpermeable or of such a nature that they do not adsorb or occlude solute, nor otherwise prevent their total solute quantity from fully and readily dissolving in the entrained solvent. Secondly, adequate time and suitable conditions are assumed to be available during each extraction treatment to assure that the concentration of the solute in the entrained liquor has adjusted itself to equal the concentration in the surrounding extracting solution. In other words, after each treatment with liquid, the total solute associated with the solids is in solution, and the solute concentration in the entrained liquid is equal to that in the surrounding liquid.

Thus, for the first extraction treatment:

$$S_1/W_1 = s_1/w_1 \quad \text{or} \quad S_1/s_1 = W_1/w_1$$

also:

$$S_2/W_2 = s_2/w_2 \quad \text{or} \quad S_2/s_2 = W_2/w_2$$

Then:

$$S_1 = (W_1/w_1)s_1 = a_1s_1 \quad \text{and} \quad S_2 = (W_2/w_2)s_2 = a_2s_2 \quad (5)$$

The constants  $a_1$  and  $a_2$  are equal to the ratios of liquid withdrawn to liquid retained for their respective extractions. Similar relations apply to subsequent treatments where equilibrium is attained.

As a third assumption, the weights of the entrained solutions remaining in the solids after every treatment are considered constant and equal, or  $w_1 = w_2 = \dots = w$ , a constant. From this assumption and the assumption that in every treatment the charge is submerged in equal weights of liquid, it can be readily seen that equal weights of extract liquid are withdrawn after each extraction, or  $W_1 = W_2 = \dots = W$ . Then:

$$W_1/w_1 = W_2/w_2 = W/w \quad \text{or} \quad a_1 = a_2 = \dots = a \quad (6)$$

where  $a$  is the constant ratio of withdrawn to entrained liquid, equal for every extraction.

These last two assumptions are attainable in many operations and are reasonable where the extracting operations do not change the physical characteristics of the solids and where the properties of the extract liquids are not appreciably affected by the various quantities of solute dissolved in them over the actual concentration range involved.

It also follows from the constancy of the entrained solution quantities that, except for the first extraction where  $w_0$  can be any value, the inflowing extracting solutions are equal to  $W$ . For this exception, the inflowing solution to the first extraction is, from equations (2) and (6):

$$W_F = W_1 + w_1 - w_0 = W + (W/a) - w_0$$

or:

$$W_F = W[(a+1)/a] - w_0 \quad (7)$$

Where the original charge is not wet with solvent,  $w_0 = s_0$ .

Lastly, assume that the inflowing liquids for every extraction are solute-free solvents, or  $S_F = S_G = 0$ . Then, from equations (1), (5), and (6):

$$s_0 = S_1 + s_1 = as_1 + s_1 = (a+1)s_1$$

or:

$$s_1 = s_0/(a+1) \quad (8)$$

Likewise, from equations (3), (5), and (6):

$$s_2 = s_1/(a+1)$$

and on substituting the value of  $s_1$  from equation (8):

$$s_2 = s_0/(a+1)^2$$

By continuing this method of material balances and substitution, it can be developed that:

$$s_n = s_0/(a+1)^n \quad (9)$$

Here  $s_n$  is the solute quantity in the solids charge after  $n$  extraction treatments with solvent,  $s_0$  is the original quantity of solute in the charge, and  $a$  is the ratio of extract solution withdrawn to solution retained by the solids after each extraction treatment.

**Illustrative Problem.** A batch extractor is charged with 7000 lb. of meat cracklings, containing 15% tallow. Extraction of the tallow is accomplished by filling the extractor with heptane solvent and then draining. Three solvent treatments are given to the charge, and 3500 lb. of extract liquid are drawn off each time. The total weight of drained, solvent-wet solids after the third extraction is 8500 lb. The ideal conditions are assumed where the total tallow content of the cracklings goes into solution during the first treatment, and a uniform, equilibrium concentration of tallow in the heptane is obtained in each extraction treatment before draining. The weight of entrained solution in the cracklings after each extraction is taken as constant. No allowance is made for solids fines drawn off with the extract liquid.

(1) What is the minimum attainable tallow content in the drained cracklings after the third heptane treatment under the optimum, ideal extraction conditions?

(2) What would be the average tallow concentration in the total extract liquid or miscella?

**Solution.** (1) The original tallow content of the cracklings is:

$$15\% \text{ of } 7000 \text{ lb.} = 1050 \text{ lb.}$$

The weight of tallow-free cracklings then is:

$$7000 - 1050 = 5950 \text{ lb.}$$

The entrained weight of solution,  $w$ , after each drainage is equal to the difference between the total weight of discharged solids with solution and the weight of the solute- and solvent-free solids, or:

$$w = 8500 - 5950 = 2550 \text{ lb.}$$

The weight ratio of solution withdrawn to solution retained by the solids for each extraction treatment is:

$$a = W/w = 3500/2550 = 1.372$$

From equation (9), the tallow content of the cracklings after the third heptane extraction is:

$$s_3 = 1050/(1.372 + 1)^3 = 1050/13.35 = 78.7 \text{ lb.}$$

Then the per cent tallow content in the solvent-free extracted cracklings is:

$$78.7/(78.7 + 5950) = 1.30\%$$

In actual extraction of meat cracklings where the preparation does not make all tallow readily soluble, and where the equilibrium concentrations are not obtained, tallow contents of 3–4% are normally left in the extracted cracklings after three treatments.

(2) From a material balance or equation (7), where  $w_0 = s_0$  for the solvent-free original cracklings, the heptane quantity used to submerge the cracklings for the first solvent treatment is:

$$\begin{aligned} W_p &= W[(a + 1)/a] - s_0 \\ &= 3500(2.372/1.372) - 1050 \\ &= 6050 - 1050 = 5000 \text{ lb.} \end{aligned}$$

In each of the other extractions, since the entrained liquid weight is constant, solvent added equals the weight of solution withdrawn, or 3500 lb.

Total tallow in the extract liquids or miscellas is the solute difference between the original charge and the finally extracted cracklings discharged, or:

$$1050 - 78.7 = 971.3 \text{ lb.}$$

Then the concentration of the combined extract liquids drawn off from the extraction vessel is:

$$\frac{971.3 \times 100}{5000 + 3500 + 3500} = 8.1\%$$

#### MULTIBATCH EXTRACTION

The approach to the theory of multibatch extractions is very similar to the procedures for single-batch extraction. Each solids charge of the battery of vessels can be considered as a single batch, and material balances can be made for each solvent treatment of that charge, using diagrams and equations similar to those previously presented under the general methods for single-batch extraction theory. The discussion there on the relationships of the solute content and the entrained solution quantity in the solids charge to the other operating variables and conditions of the extraction also applies for each extraction treatment of the multibatch system.

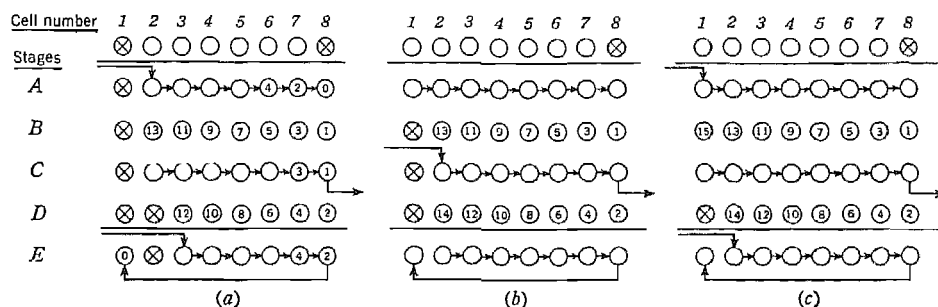
In addition, in multibatch operations, relationships can be readily set up between the charges in the battery and the liquid quantities flowing to and from each charge, since the solution withdrawn from one charge serves as the inflowing extracting liquid for a succeeding charge, and since each charge in the batch usually passes through the same extraction steps in a set time cycle that every other charge of the batch does. Therefore, with the minimum of known quantities of solids and liquids entering the multibatch system in a given flow sequence and time cycle, and with certain relations set or determined between quantities within the system, equations can be set up and solved for such an extraction system. Again, as in the single-batch method, the extraction principles are most readily applied to intermittent drainage operations.

The most effective and universally used method is the true countercurrent extraction. Here each freshly filled charge is subject to the same number of treatments of extracting liquid quantities of successively decreasing solute contents until the charge in its last extraction treatment, before being discharged from the system, is contacted with the fresh incoming solvent. Likewise, the successive solvent portions entering the battery first contact the most extracted solids before their discharge, then flow in regular sequence from vessel to vessel to contact solids charges of increasing

solute content, until the liquids enter and are withdrawn as concentrated solution portions from the vessels containing the freshly charged solids.

**Number of Treatments.** The most confusing and frequently misunderstood concept is the relationship between the number of solvent treatments of each solids charge and the number of vessels or cells in the extraction battery. The following discussion, based on the work of Hawley (7), will develop and present this relationship and its tie-in with the time cycle of the multibatch operation on the countercurrent principle.

In an earlier discussion, illustrated by Figure 3, one method of operating an eight-cell multibatch system was described. The method is diagrammatically represented by the successive operations in Figure 11(a). Here are represented the successive liquid-flow stages between cells that alternate with static extraction stages. Figures 11(b) and (c) represent two other ways in which an eight-cell battery can be operated countercurrently.



- denotes cells containing or receiving extracting liquid (enclosed figures indicate number of liquid-extracting treatments applied).  
 ⊗ denotes cells drained of extracting liquids, either freshly filled with solids charge or discharging extracted solids.  
 → denotes transfer of extracting liquid between cells, introducing fresh extracting liquid into the battery, or withdrawing final extract liquid from battery.

Fig. 11. Diagrams for multibatch countercurrent extraction in an 8-cell battery. (Number of solvent treatments per solids charge: (a) 13; (b) 14; (c) 15.)

It can be seen that there are two distinct types of operation for a countercurrent multibatch system. The first type (type one) is the operation where liquid inflow to the system and liquid withdrawal from the system are accomplished during different liquid-transfer periods, as illustrated by stages A and C of Figures 11(a) and (c). The other type of operation (type two) is illustrated in Figure 11(b) where liquid inflow to and discharge from the system are done during the same liquid-transfer period, as shown in stage C, alternating with period of liquid transfer between cells without extracting liquid entering or leaving the system as a whole, as shown by stages A or E.

There are variations from these two types of operation that may be used in special cases to increase or decrease the number and time of treatments for a given extraction battery. Some of these variations deviate from true countercurrent flow. As an example, the operation illustrated by Figure 11(b) can be modified so that two successive transfer stages of liquid inflow and withdrawal for the same cells, as in stage C, alternate with a single intercell transfer stage, as in A or E. Use of such duplicated inflow-discharge stages increases the number of treatments by 50%.



Such variations can be analyzed in a manner similar to the development of the equations for the two basic types of operation as of Figure 11.

To determine the number of treatments as related to the number of cells consider, in Figure 11(a), cell 8 in stage A just filled with a fresh charge of solids and being contacted with the liquid from cell 7. The first treatment is accomplished in the extraction stage B. In stage C, liquid from cell 8 is then withdrawn from the system, and this cell is again filled with liquid from cell 7 and undergoes a second extraction treatment in stage D. In stage E, liquid is transferred from cell 8 to cell 1 and another liquid quantity from cell 7 fills cell 8.

It will be noted that cell 8 in stage E has the same relative position in the battery, as to liquid flow, as cell 7 in stage A. Therefore, rather than continue the illustrative treatments of cell 8 in the diagram lengthily down the page, the liquid-transfer step for cell 8, after the second treatment, can be represented in stage A in the position of cell 7, and the illustrative operations continued from there.

Considered in the transposed position in A, cell 8 is drained and then filled with liquid from the adjacent cell. Its third extraction is completed in stage B. It is subjected to liquid transfer in stage C and receives a fourth extraction in stage D. The position of this material from the fourth extraction in stage E, in relation to liquid flow, is the same as that for cell 6 in stage A, so attention can be transferred to that position in stage A to represent cell 8 after the fourth treatment. In this manner, the treatments in cell 8 can be followed through the equivalent positions for the successive cells in the first few stages of the operation.

Thus, from the diagram can be developed 13 relative positions of cell 8 during the full extraction cycle, as numbered in stages B and D, each position representing the completion of an extraction treatment. Also to be noted are the three consecutive extraction periods in the cycle when cell 8, represented in positions of cell 2 in stage D, cell 1 in stage B, and cell 1 in stage D, is drained of liquid and available for discharge of extracted solids and refilling with fresh solids for the next extraction cycle.

A similar step-by-step follow-through can be used to determine the number of liquid treatments for each cell in Figures 11(b) and (c).

Generally, let  $d$  be an integral number representing the number of cells filled with extracting liquid after a transfer stage involving liquid addition to the system. Then, for type one extraction, as illustrated in Figures 11(a) and (c) where liquid fill and withdrawal are in separate steps,  $d$  will be the number of cells being treated with liquid in stage B after the addition of liquid to the system, and  $d - 1$  will represent the number of cells treated in the extraction stage D after the withdrawal of liquid and transfer between cells.

The number of cells treated for these two successive extraction stages will be  $d + (d - 1) = 2d - 1$ , which also represents the number of liquid treatments that cell 8 or any other cell of the system will get in a complete extraction cycle. It will be noted that, since  $d$  is an integer, the number of treatments per charge for this type of operation is an odd number.

Likewise, as shown in Figure 11(b), the number of liquid-filled cells in stage D after adding fresh liquid to the system is  $d$ , and the number in the next extraction stage, where liquid is transferred between cells without being added to or leaving the system (see stage B), is also  $d$ . The number of treatments for type two extraction is then  $2d$ , which is always an even number.

Therefore, it can be concluded that, for the countercurrent multibatch extraction

where the liquid addition to the system is made during a separate liquid-transfer period than the liquid withdrawal from the system, the number of liquid treatments for each charge,  $t$ , is an odd number, equal to one less than twice the number of cells filled after the liquid-addition and transfer steps are complete, or  $t = 2d - 1$ .

For the countercurrent multibatch extraction where the liquid addition to the system and the liquid withdrawal are accomplished during the same liquid-transfer period, the number of treatments will be an even number, equal to twice the number of cells filled with liquid after this liquid-addition stage is complete, or  $t = 2d$  for this case.

**Interval Between Consecutive Discharges from or Additions to System.** There will be an interval of 4 stages before repeating, on a successive cell, a given operation that adds or removes material from the battery system, whether it is solids charging or discharge, liquid addition to or withdrawal from the battery. This interval encompasses the equivalent of two extraction and two liquid-transfer stages. If  $b$  is the time interval for the extraction stage and  $P$  is the time interval for the liquid-transfer stage, then the interval between repeating an addition or removal operation in the system is:

$$I = 2b + 2P \quad (10)$$

Where the liquid movements to and from the cells are done simultaneously, as in full immersion methods of extraction, the transfer is done in one step, and the total transfer time,  $P$ , is also the time of liquid transfer for each cell.

However, in the intermittent drainage methods of extraction, the liquid from one cell at a time is removed before it is refilled with liquid. Here the time  $P$  is the sum of the time intervals for each liquid-transfer step of the stage. Thus, in type one operations, in the transfer stage  $A$ , there are  $d - 1$  steps where liquid is transferred from cell to cell, followed by one step to fill a cell of the system, or a total of  $d$  steps. In stage  $C$ , there is a step to withdraw liquid from the system followed by a series of  $d - 1$  steps to transfer liquid from cell to cell, or again a total of  $d$  steps. Therefore, for each transfer stage there are  $d = (t + 1)/2$  steps. Then, if  $p$  is the time interval for each transfer step:

$$P = [(t + 1)/2]p \quad (11)$$

and:

$$I = 2b + (t + 1)p \quad (12)$$

For type two extraction, as represented in Figure 11(b), there will be in stage  $C$ , one liquid discharge from the system,  $d - 1$  intercell transfers of liquid, and one step for adding liquid to the system, or  $d + 1$  total steps. In stage  $A$ , there will be  $d$  transfer steps for liquid from cell to cell. Then  $2P$  for consecutive pumping stages will be equal to  $(2d + 1)p$  or  $(t + 1)p$ , since  $t = 2d$  for type two extractions. Therefore,  $I = 2b + (t + 1)p$ , the same equation as for type one extractions.

The total cycle time,  $T$ , will be this interval times the number of cells, or:

$$T = cI \quad (13)$$

where  $c$  is the number of cells in the battery.

**Time Interval for Discharge and Refill of Solids.** Since, as previously indicated, each of the cells in stages  $B$  and  $D$  can represent the position, in regard to liquid flow

and extent of solids extraction, of each cell in the successive stages of a complete extraction cycle, there will be a total of  $2c$  of these positions, where  $c$  is the number of cells. Since  $t$  is the number of successive treatments for a given cell,  $2c - t$  equals the number of positions of the cell where it is not being treated with liquid and is available for solids discharging and recharging.

Then,  $2c - t$  represents the number of extraction periods in the time interval in the period after draining a cell for solids discharge and before running liquid into this cell, loaded with a fresh charge. Between each of the  $2c - t$  extraction periods is a liquid-transfer period, or there will be one less transfer period than extraction periods, or  $2c - t - 1$  transfer periods. Then the total interval,  $\theta_0$ , for discharge and refill of solids is given by:

$$\theta_0 = (2c - t)b + (2c - t - 1)P \quad (14)$$

which can be used directly for full immersion extraction.

In type one extraction by the intermittent drainage method, the number of liquid-transfer steps for either the filling or discharge transfer stages will be equal to  $d$ , or  $(t + 1)/2$ . Therefore:

$$\theta_0 = (2c - t)b + (2c - t - 1)(t + 1)p/2 \quad (15)$$

for type one extraction, that is, when  $t$  is an odd number.

For type two extraction, since  $t$  is an even number, the number of transfer stages,  $2c - t - 1$ , is odd. Since the cell being prepared for solids discharge is drained of liquid by a cell-to-cell transfer stage, the first transfer stage during which this cell is unloaded of solids is a liquid fill and discharge stage. Therefore, there will be one more fill and discharge stage during the cell discharge and reloading with solid than for the alternating stages of intercell transfer, or there will be  $c - (t/2)$  stages, each having  $d + 1 = (t/2) + 1$  transfer steps alternating with  $c - (t/2) - 1$  stages of cell-to-cell transfer only, each having  $d = t/2$  steps. Therefore, the total number of transfer steps will be:

$$[c - (t/2)][(t/2) + 1] + [c - (t/2) - 1][t/2] = [2c - t - 1][(t + 1)/2] + 1/2 \quad (16)$$

Then:

$$\theta_0 = (2c - t)b + [(2c - t - 1)(t + 1) + 1]p/2 \quad (17)$$

when  $t$  is even.

**Actual Extraction Time Per Treatment.** The actual extraction time of a charge in a cell for each liquid treatment is taken as the period from the instant that the filling of the cell with liquid is completed to the instant when draining of that cell is started. For simultaneous liquid transfer, this actual time is the duration of the extraction stage only, and is equal to  $b$ . However, when the liquid movement is done in steps, the cells are filled and drained at different times during the liquid-transfer stage and some extra extraction is accomplished in the liquid-filled cells during that stage.

In type one extractions (for example, in Figures 11(a) and (b)) there are  $d$  cells to be filled in stage  $A$ . After the first is filled, it awaits the filling of  $d - 1$  more cells, or its extraction time during stage  $A$  is  $(d - 1)p$ . This first cell has the regular extraction period of time  $b$  in stage  $B$ , and is immediately drained in stage  $C$ . Its total actual extraction time for this treatment is, therefore,  $b + (d - 1)p$ .

Likewise, the second cell to be filled in stage *A* awaits the filling of  $d - 2$  more cells for an extra extraction time of  $(d - 2)p$ . Then, after a regular extraction period  $b$ , this cell awaits draining of the first cell before being drained itself after a period  $p$  in stage *C*. Thus, the total actual extraction time for this second cell is also  $b + (d - 1)p$ .

The last cell filled in stage *A* has no extra extraction time in that stage, undergoes the regular extraction period  $b$  in stage *B*, and in stage *C* awaits the draining of  $d - 1$  cells before it is itself drained after an extra extraction period of  $(d - 1)p$  in that stage. Again, the actual extraction time totals  $b + (d - 1)p$ , which applies, in all type one operations, to cells filled in the transfer stages that add liquid to the system.

In type one operations, the cells, filled in transfer stages where liquid is withdrawn from the system, each undergo an actual extraction period before draining of  $b + (d - 2)p$ , as can be seen by studying the liquid-transfer steps in stages *C* and *E* of Figures 11(a) and (c).

In a full extraction cycle of an odd number of treatments,  $t = 2d - 1$ , there are  $d$  treatments (the odd-numbered ones) that follow after a liquid addition to the system. Alternating with each of these treatments is one of the  $d - 1$  treatments (the even-numbered ones) that follow after a liquid withdrawal from the system. Therefore, there are, in the full extraction cycle for a charge,  $d$  treatments, each having an actual extraction time of  $b + (d - 1)p$ , and  $d - 1$  treatments, each having an actual extraction time of  $b + (d - 2)p$ . Thus, the sum of the actual extraction times for the treatments of the cycle is:

$$d[b + (d - 1)p] + (d - 1)[b + (d - 2)p] = (2d - 1)b + 2(d - 1)^2p \quad (18)$$

Since  $t = 2d - 1$ , equation (18) becomes  $tb + p(t - 1)^2/2$ , the total actual extraction time for  $t$  treatments. The average actual extraction time per cell would then be the above divided by  $t$ , or:

$$\theta_E (\text{av.}) = b + p(t - 1)^2/2t \quad (19)$$

Summarizing for type one extraction, where there is an odd number of treatments:

(1) There will be  $d = (t + 1)/2$  treatments, the odd-numbered ones, that will have an actual extraction time of  $\theta_E = b + (d - 1)p = b + p(t - 1)/2$ .

(2) There will be  $d - 1 = (t - 1)/2$  treatments, the even-numbered ones, that will have an actual extraction time of  $\theta_E = b + (d - 2)p = b + p(t - 3)/2$ .

(3) The average actual extraction time per treatment will be  $\theta_E (\text{av.}) = b + p(t - 1)^2/2t$ .

For type two extraction, there are in the cycle of  $t$  treatments per cell  $d$  treatments after transfer stages in which liquid is both added and withdrawn from the system, and  $d$  treatments after the alternating transfer stages where only intercell movement of liquid occurs. From a study of Figure 11(b) it will be seen that in either kind of treatment the number of extra extraction periods a liquid-filled cell undergoes before being drained is equal to  $(d - 1)p$ , or the total actual extraction time for each cell during a treatment is:

$$\theta_E = b + (d - 1)p = b + p(t - 2)/2 \quad (20)$$

for type two extraction where  $t$  is an even number.

It will be noted in these derivations that no allowance is made for any extraction time that may occur in a cell partly filled with liquid during the filling or draining of

TABLE I. Summary of Equations for Multibatch Countercurrent Operation.

*Stepwise Liquid Transfer for Cells.*

Type one operations: Liquid addition to system in one transfer stage and liquid withdrawal from system in alternating transfer stage.	Type two operations: Liquid addition to and withdrawal from system in the same transfer stage, which alternates with a transfer stage of intercell liquid movement only.
$t$ is <i>odd</i> $t = 2d - 1$	$t$ is <i>even</i> $t = 2d$
$\theta_0 = (2c - t)b + (2c - t - 1)(t + 1)p/2$	$\theta_0 = (2c - t)b + [(2c - t - 1)(t + 1) + 1]p/2$
$\theta_E = b + p(t - 1)/2$ for odd-numbered treatments	
$\theta_E = b + p(t - 3)/2$ for even-numbered treatments	$\theta_E = b + p(t - 2)/2$
$\theta_E (\text{av.}) = b + p(t - 1)^2/2t$ average per treatment	

For either type of operation:

$$I = T/c = 2b + (t + 1)p$$

*Simultaneous Liquid Transfer for Cells.*For either type of operation ( $t$  determined as above):

$$\theta_0 = (2c - t) + (2c - t - 1)P$$

$$\theta_E = b$$

$$I = T/c = 2b + 2P$$

**Nomenclature**

$d$	= number of liquid-filled cells after transfer stage involving liquid addition to system
$t$	= number of liquid treatments on a solids charge in complete extraction cycle
$c$	= number of cells in system
$b$	= extraction time during which there is no liquid transfer in system
$p$	= time to complete a filling or draining of a cell
$P$	= total time to complete a liquid-transfer stage in the system
$T$	= total time to complete a full extraction cycle on a solids charge
$f$	= time interval between a consecutive addition or withdrawal operation
$\theta_0$	= total time a cell is drained of liquid and available for discharging and refilling of solids
$\theta_E$	= actual extraction time on a solids charge between liquid-transfer operations

that cell. Since, for each treatment a transfer period,  $p$ , is required for each of the operations of filling and draining a cell, there will be, during the  $t$  treatments of the full cycle for each cell, a cumulative period of time equal to  $2tp$ , when there is liquid transfer to and from the cell, for which no actual extraction time is assumed.

Table I summarizes these equations involving number of treatments and time intervals in multibatch countercurrent extraction.

**Illustrative Problem.** A battery of 5 vessels is used in the hot-water extraction of cascara sagrada bark by multibatch countercurrent extraction, using the intermittent drainage method. The pumping times to fill a vessel containing the bark with fresh hot water, to draw off cascara extract liquor from the battery, and to drain a vessel to refill another vessel are 2 minutes each. A total ex-

traction cycle is completed in 2 hours. The extract-liquor draw-off from the battery and the fresh-water fill are done in the same series of pumping steps. After completing such a liquid transfer, there are 3 vessels filled with liquid. Of the other 2 vessels, one has just been drained and is ready for discharge, and the other is being filled with fresh bark.

- (1) What is the number of treatments given each charge of bark?
- (2) What is the period of extraction time when no liquid pumping is going on in the battery?
- (3) What is the time available after draining a vessel for unloading the exhausted bark and refilling with fresh bark?
- (4) What is the actual extraction time on a charge of bark after submerging with liquid until draining of that liquid is started?
- (5) How can the same battery be operated to increase the number of treatments without changing the total time for the extraction cycle or the pumping time per transfer step?

TABLE II. Extraction Times for Multibatch Countercurrent Operation of a 5-Vessel Battery.<sup>a</sup>

	Number of treatments per charge			
	9	8	7	6
Nonpumping extraction period, $b$ , minutes.....	2	3	4	5
Solids discharge and reloading time, $\theta_0$ , minutes.....	2	16	28	42
Actual extraction time, for each treatment, $\theta_E$ , minutes.....	$\begin{cases} 10^b \\ 8^c \\ 9\frac{1}{9} \text{ (av.)} \end{cases}$	9	$\begin{cases} 10^b \\ 8^c \\ 9\frac{1}{7} \text{ (av.)} \end{cases}$	9
Total extraction time for each charge, $t\theta_E$ , minutes.....	82	72	64	54

<sup>a</sup> 2-hour extraction cycle and 2 minutes for each liquid-pumping step.

<sup>b</sup> For each of the odd-numbered treatments.

<sup>c</sup> For each of the even-numbered treatments.

**Solution.** (1) Since withdrawal of extract liquor and addition of fresh water to the battery occurs in the same series of transfer steps, and since there are 3 vessels filled after this transfer of liquid, the number of treatments,  $t$ , is even and equal to  $2d$ . Since  $d = 3$ , the number of filled cells after the transfer involving liquid addition,  $t = 6$  treatments per solids charge.

(2) The extraction time,  $b$ , where no pumping occurs, is found from the equation:

$$T = T/c = 2b + (t + 1)p$$

where the extraction time  $T$  equals 120 minutes,  $c = 5$  cells or vessels in the battery, and  $p$ , the time for a pumping step, is 2 minutes. Then,  $120/5 = 2b + (6 + 1)2$ , or  $b = 5$  minutes.

(3) The time available for discharging and reloading bark for each vessel is given by equation (17):

$$\theta_0 = (2c - t)b + [(2c - t - 1)(t + 1) + 1]p/2$$

for type two operations where  $t$  is an even number. Therefore:

$$\theta_0 = (2 \times 5 - 6)5 + [(2 \times 5 - 6 - 1)(6 + 1) + 1]2/2$$

or:

$$\theta_0 = 20 + 22 = 42 \text{ minutes}$$

(4) The actual extraction time for each treatment of a charge is given by equation (20):

$$\theta_E = b + p(t - 2)/2$$

where  $t$  is an even number, or:

$$\theta_E = 5 + 2(6 - 2)/2 = 9 \text{ minutes}$$

(5) Operations can be changed so that there are 4 liquid-filled vessels and 1 drained vessel after each transfer stage that involves liquid addition to and withdrawal from the battery. In this case,  $d = 4$  and the treatments are  $t = 2d$  or 8. Liquid-transfer operations can be changed so that the liquid withdrawal and the fresh water fill occur in different transfer stages. In this case, if operations are such that all 5 vessels are filled after each transfer stage involving fresh-water fill,  $d = 5$  and  $t = 2d - 1$  or 9; and if only 4 cells are filled after such transfer stages,  $d = 4$  and  $t = 7$ .

On substituting the number of treatments in the appropriate equations of Table I, Table II can be made from the results of the calculations.

**Development of Flow Diagrams.** Referring again to Figure 11(a), one can see that the cell freshly charged with solids, cell 8 in stage A, is filled with liquid drained from an adjacent cell whose charge has already received two liquid treatments.

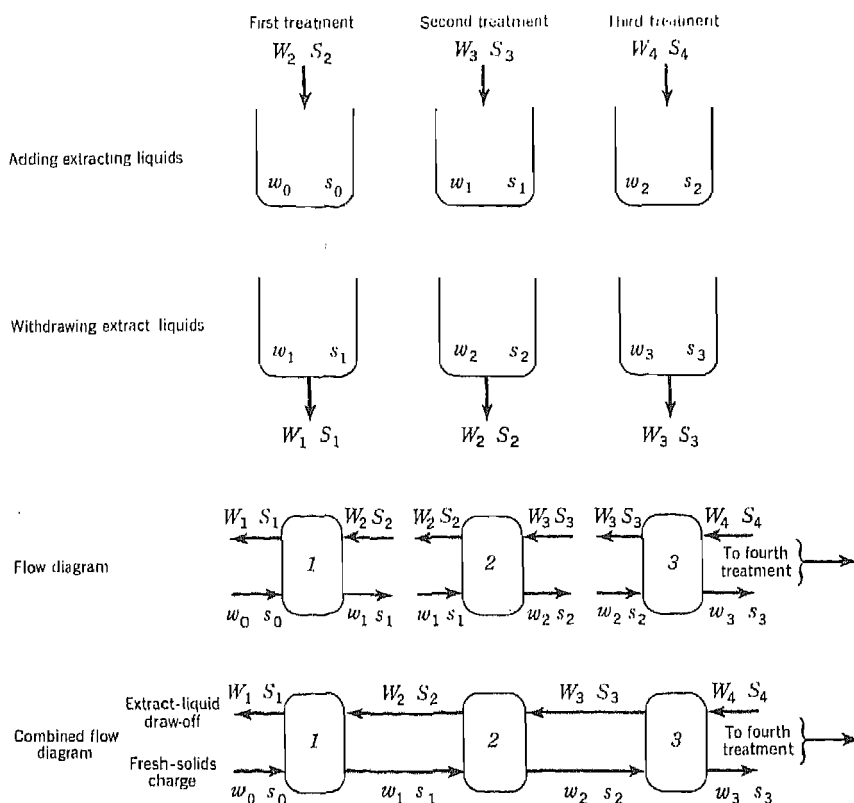


Fig. 12. Relative movement of material in countercurrent multibatch extraction.

The top-left diagram of Figure 12 represents the state of affairs in the cell freshly charged. The original solids charge contains a quantity of solute  $s_0$  and a quantity of solute plus solvent of  $w_0$ , and the inflowing liquid  $W_2$  contains  $S_2$  solute.

After the first extraction treatment; the cell is drained, as shown for cell 8 at the start of stage C, and leaves  $w_1$  solute plus solvent and  $s_1$  solute in the solids charge with the drained solution withdrawn from the system of  $W_1$  containing  $S_1$  solute. This is represented in the first diagram of the second row in Figure 12. Row three represents the relative flow of materials for this first treatment.

In the middle vertical column of Figure 12 are shown the liquid addition (as for cell 8, stage C, of Figure 11(a)), the liquid withdrawal (see cell 8, stage B, Figure 11(a)),

and the relative flow diagram for the second treatment of the charge where  $W_3$  and  $S_3$  are inflowing solution and solute quantities of liquid, drawn off from the third extraction of another cell,  $w_1$  and  $s_1$  are quantities left in the solids from the first treatment, and  $w_2$  and  $s_2$  are quantities remaining in the solids drained after the second treatment.  $W_2$  and  $S_2$  are quantities in the liquid drained from this second extraction which are equivalent to those added in the first treatment and which are also added to a cell freshly charged with solids.

Likewise, the last column represents the third extraction with inflowing liquid,  $W_4$ ,  $S_4$ , drained from a fourth treatment and the outflowing liquid,  $W_3$ ,  $S_3$ , that will be used as inflowing liquid for the second treatment of another cell. Similarly, all of the  $t$  treatments of the extraction cycle can be represented and their flows interrelated.

The individual flow diagrams show relative flows of liquid as well as solids into and out of each treatment. These diagrams can be combined to get a single flow diagram, as at the bottom of Figure 12, that well represents the cyclic treatments of batches of solids and interrelates equivalent flows. This combined flow diagram is practically the same as that shown for continuous extraction in Figure 13, where the total treatments are designated by  $m$  instead of  $t$ .

This flow analogy of continuous to multibatch extraction will be exploited later as equations derived for continuous extraction will be shown there to apply directly to multibatch extraction with only slight modifications of concept.

#### CONTINUOUS EXTRACTION

The material-balance approach used in single-batch and multibatch extractions is similarly applied to continuous extraction. The movement of solids through the system in constant or interrupted contact with the liquids is a requirement for con-

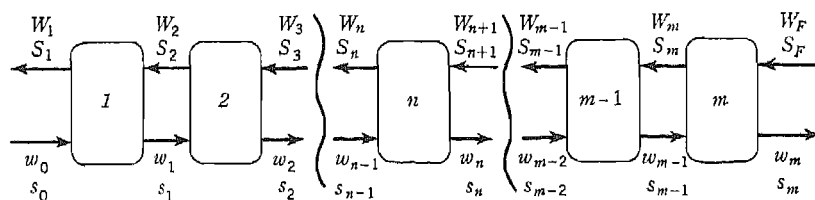


Fig. 13. Flow diagram for continuous countercurrent extraction.

tinuous operation. The flows of liquid and solids are countercurrent for most effective extraction. The intermittent drainage method of extraction is here also the one to which material balances can most effectively be applied.

For such extraction, the system is considered as made up of a series of units, either separate vessels, or a number of cells or sections in a single piece of equipment. Separation of solids from the bulk of the liquids by drainage or thickening is accomplished between the units. In each unit, a solvent application is given to a solids charge, analogous to the treatment on a charge in a single-batch vessel, or in a cell in a multibatch battery.

Figure 13 represents such a continuous extraction system made up of  $m$  units or sections. Here, the meanings of the letters are almost the same as previously used for noncontinuous operations, the only difference is that the flow quantities are weights



per unit of time or per given quantity of inflowing solids rather than weights per solids charge. Indeed, the derivations of equations to be obtained for continuous extraction can be used without other changes for multibatch extraction with an equal number of treatments by using the quantities as weight per charge.

The overall material balance of counterflowing quantities for the  $m$  cells in Figure 13 is given by:

$$S_F + s_0 = S_1 + s_m \quad (21)$$

$$W_F + w_0 = W_1 + w_m \quad (22)$$

Material balances can be made from cell to cell, to determine the quantities leaving and entering each cell. For instance, for cell 1:

$$S_2 + s_0 = S_1 + s_1 \quad (23)$$

$$W_2 + w_0 = W_1 + w_1 \quad (24)$$

If  $W_1$ ,  $S_1$ ,  $w_0$ , and  $s_0$  are known or can be determined from the overall material balances, equations (21) and (22), then by determining or fixing  $s_1$  and  $w_1$  or relating them to other quantities such as the concentration of the solution leaving cell 1, that is  $S_1/W_1$ , one can solve for  $W_2$  and  $S_2$ . Then, with  $W_2$ ,  $S_2$ ,  $w_1$ , and  $s_1$  known, and on determining or finding relationships for  $w_2$  and  $s_2$ ,  $W_3$  and  $S_3$  can be solved for in the material-balance equation for cell 2. In this manner, the solution and solute quantities in the solids and extracting liquid can be determined by stepwise material balances from cell to cell to the  $m$ th or last cell.

This approach has been used by many in presenting solutions for countercurrent continuous extraction. Armstrong and Kammermeyer (1) present a step-by-step method of graphical solution. It is based on the consideration that solute and solvent plus solvent quantities leaving a cell with the solids are known functions, experimentally determined, of the solute concentration of the liquid leaving that cell.

Ruth (9) offers a semigraphical method in which solute quantities and solvent and solute quantities in a solids leaving a cell have been experimentally determined, and can be graphically plotted as a function of the solute concentration in the extracting liquid leaving that cell. He gives consideration to a solute quantity in the drained solids that is occluded or absorbed, or otherwise not in equilibrium with the extracting liquid.

Generally, earlier published methods have assumed that the total solute in the solids dissolves completely in the entrained liquid and that equilibrium conditions are attained in each cell, so that solute concentration of the entrained solution in the solids leaving a cell is the same as the solute concentration in the outflowing extracting liquid. Thus, Ravenscroft (8) in his graphical stepwise method plots entrained solution and solute quantities in the solids against the solute concentration, which is considered the same for the entrained liquid in the solids and the outflowing extracting liquid. He applies this method to the multiple extraction of a single batch, to multibatch countercurrent extraction, and to continuous countercurrent extraction. Elgin (6) uses the triangular graphical method analogous to that for liquid-liquid extraction. He also assumes equal solute concentrations in the solids-entrained solution and in the outflowing liquid, and entrainment quantities for each extraction step that may or may not be equal. Baker (3) presents a general algebraic method where solids-entrained solutions and outflowing extracting solutions have the same solute concen-

tration after extraction in each cell, but where the ratio of outflowing liquid weight to weight of entrained solution in solids can be expressed as a constant, differing for each cell. He also considers the cases where the ratio of outflowing liquid to entrained liquid weights are the same constant for the cells of the system.

**Equilibrium Conditions.** As for batch extraction, ideal conditions are set up for derivations after the methods of Baker that have been effectively presented by Badger and McCabe (2). Assume total solution of the solute of the solids in the entrained liquor. Assume also equilibrium conditions; that is, the solute concentration in the entrained liquid leaving each cell with the solids is the same as that in the outflowing liquid from that cell. Then:

$$S_n/W_n = s_n/w_n \quad \text{or} \quad S_n/s_n = W_n/w_n \quad (25)$$

where  $n$  is any cell number from 1 to  $m$ .

On the assumption that the solids leaving any cell have a constant weight of entrained solution,  $w_1 = w_2 = \dots = w_n = \dots = w_m = w$ , a constant. This equality does not necessarily apply to  $w_0$ , as solids entering the system may contain any quantity of solvent or be solvent-free. From material balances over every cell but the first, it can be seen that  $W_2 = W_3 = \dots = W_n = \dots = W_m = W_F = W$ . Then:

$$W_n/w_n = W/w = a \quad (26)$$

where  $a$  is a constant and  $n$  is any cell number from 2 to  $m$ . From equations (25) and (26):

$$S_n/s_n = a \quad \text{or} \quad S_n = as_n \quad (27)$$

for any value of  $n$  except where  $n = 1$ . For  $n = 1$ :

$$S_1/s_1 = W_1/w_1 = a_1 \quad \text{or} \quad S_1 = a_1s_1 \quad (28)$$

where  $a_1$  is a ratio not necessarily equal to  $a$ .

*Derivation of General Equation.* For a material balance of solute over cell  $m$ :

$$s_{m-1} = s_m + S_m - S_F \quad (29)$$

or applying equation (27):

$$s_{m-1} = s_m(1 + a) - S_F \quad (30)$$

For a material balance over cells  $m$  and  $m - 1$ :

$$s_{m-2} = s_m + S_{m-1} - S_F = s_m + as_{m-1} - S_F \quad (31)$$

On substituting the value of  $s_{m-1}$  from equation (30):

$$s_{m-2} = s_m + a[s_m(1 + a) - S_F] - S_F = s_m(1 + a + a^2) - S_F(1 + a) \quad (32)$$

For a material balance over the last three cells:

$$s_{m-3} = s_m(1 + a + a^2 + a^3) - S_F(1 + a + a^2)$$

Then:

$$s_{m-(m-1)} = s_1 = s_m(1 + a + a^2 + \dots + a^{m-1}) - S_F(1 + a + a^2 + \dots + a^{m-2}) \quad (33)$$

Since the factors in parentheses on the right side of equation (33) are geometric progressions, they can be expressed in the equation as follows:

$$s_1 = s_m \frac{a^m - 1}{a - 1} - S_F \frac{a^{m-1} - 1}{a - 1} \quad (34)$$

From the overall material balance for the system:

$$s_0 = s_m + S_1 - S_F = s_m + a_1 s_1 - S_F$$

or substituting from equation (34):

$$s_0 = s_m + a_1 \left[ s_m \frac{a^m - 1}{a - 1} - S_F \frac{a^{m-1} - 1}{a - 1} \right] - S_F$$

or:

$$\frac{s_0}{s_m} = 1 + \frac{a_1}{a - 1} (a^m - 1) - \frac{S_F}{s_m} \frac{a_1}{a - 1} (a^{m-1} - 1) - \frac{S_F}{s_m} \quad (35)$$

Equation (35) is a general equation expressing the ratio of the quantities of solute in the inlet and outlet solids in terms of the ratio of outflowing to entrained liquid, the number of cells, and the solute in the inflowing liquid.

*Equations for Special Conditions of Intake Materials.* If the inflowing liquid is fresh solvent, containing no solute,  $S_F = 0$ , and from equation (35):

$$s_0/s_m = 1 + (a^m - 1)(a_1)/(a - 1) \quad (36)$$

If, on the other hand,  $a = a_1$ , that is, the solids entering the system are wet with a weight of solute plus solvent equal to the weight of the entrained solution in the solids after each extraction and drainage:

$$\frac{s_0}{s_m} = 1 + \frac{a}{a - 1} (a^m - 1) - \frac{S_F}{s_m} \frac{a}{a - 1} (a^{m-1} - 1) - \frac{S_F}{s_m}$$

or:

$$\frac{s_0}{s_m} = \frac{a^{m+1} - 1}{a - 1} - \frac{S_F}{s_m} \frac{a^m - 1}{a - 1} \quad (37)$$

If both  $S_F = 0$  and  $a_1 = a$ :

$$s_0/s_m = (a^{m+1} - 1)/(a - 1) \quad (38)$$

*Derivation for Solvent-Free Solids Feed.* Frequently the case arises where the solids are fed dry, that is, where no solvent is in the solid feed, and  $w_0 = s_0$ . An equation can be derived for this where in addition there is no solute in the solvent feed, that is,  $S_F = 0$ . From equation (36):

$$a^m = [(s_0/s_m) - 1][(a - 1)/a_1] + 1 \quad (39)$$

From equation (26),  $a = W/w$  and:

$$a - 1 = (W - w)/w = (W_F - w_m)/w = (W_1 - s_0)/w \quad (40)$$

Since from equation (28)  $a_1 = W_1/w$ :

$$(a - 1)/a_1 = (W_1 - s_0)/W_1 = 1 - (s_0/W_1) \quad (41)$$

On substituting equation (41) into equation (39)

$$\alpha^m = [(s_0/s_m) - 1][1 - (s_0/W_1)] + 1$$

or:

$$\alpha^m = (s_0/s_m) - (s_0^2/s_m W_1) - 1 + (s_0/W_1) + 1 = (s_0/s_m W_1)(W_1 - s_0 + s_m) \quad (42)$$

Since from overall solute balance with  $S_F = 0$ :

$$s_0 = S_1 + s_m$$

$$\alpha^m = (s_0/s_m W_1)(W_1 - S_1) \quad \text{or} \quad \alpha^m = [s_0/s_m][1 - (S_1/W_1)] \quad (43)$$

where  $S_1/W_1$  is the concentration of the liquid flowing from the system, or:

$$s_0/s_m = \alpha^m / (1 - S_1/W_1) \quad (44)$$

**Illustrative Problem.** Consider prepared cottonseed meats containing 30% extractable oil fed to a continuous countercurrent extractor of the intermittent drainage type using hexane solvent. The drained solids, as carried over from section to section and discharged, contain 55% by weight of solution. What would be the number of theoretical sections required to reduce the extractable oil content in the meats to 0.5%, if a 20% by weight oil solution is obtained in the outflowing extract liquor or miscella? In a theoretical section all of the extractable oil in the meats is dissolved to a concentration equal to the oil concentration of the surrounding hexane solution before discharge and drainage to the next section.

**Solution.** Equation (43) is used since an oil-free hexane solvent is considered to flow into the extractor, and the prepared cottonseed meats fed to the extractor contain no solvent:

$$\alpha^m = [s_0/s_m][1 - (S_1/W_1)]$$

As a basis for calculations, take 100 lb. of oil-free cottonseed meats. Then for 30% oil in the feed:

$$s_0 = 100 \times 30 / (100 - 30) = 42.86 \text{ lb. extractable oil}$$

For 0.5% extractable oil in the solids discharge:

$$s_m = 100 \times 0.5 / (100 - 0.5) = 0.5025 \text{ lb. extractable oil}$$

Then the oil in the miscella flowing from the extractor is the difference between the oil in the feed and discharge, or:

$$S_1 = 42.86 - 0.5025 = 42.36 \text{ lb. oil}$$

For a 20% oil concentration in the miscella:

$$S_1/W_1 = 0.20$$

and therefore the weight of miscella,  $W_1$ , is:

$$W_1 = S_1 / 0.20 = 42.36 / 0.20 = 211.80 \text{ lb.}$$

Per 100 lb. of meats on an oil-free basis and a 55% solution in the drained solids, the entrained solution weight,  $w$ , is:

$$w / (100 + w) = 0.55$$

$$w = 122.22 \text{ lb.}$$

From an overall material balance, the inflowing solvent,  $W_F$ , is:

$$W_F = W_1 + w_m - w_0 = W_1 + w - s_0$$

or:

$$W_F = 211.80 + 122.22 - 42.86 = 291.16 \text{ lb.}$$

This solvent weight is equal to the weight of the liquid solution flowing out of each section except the first, or solids-feed section, or:

$$W = W_F = 291.16$$

Then,  $u = W/w = 291.16/122.22 = 2.382$ , and substituting in equation (43):

$$2.382^m = (42.86/0.5025)(1 - 0.20) = 68.23$$

$$m = \log 68.23 / \log 2.382 = 1.834 / 0.377 = 4.86 \text{ theoretical sections}$$

### Diffusional Method

Much research has been done to determine rates of transfer of solute from the solids to the surrounding liquor. Some successful results have been obtained when working with materials under highly ideal conditions, but little has been accomplished when dealing with materials under practical conditions.

By analogy to other transfer operations (such as heat distribution, drying of solids, solids dissolving in liquids, absorption and stripping of gases in liquids, and desorption and adsorption of gases in solids), certain rates-of-transfer equations have been set up for specific types of solute transfer from solids to liquid solvents.

Consideration has been given primarily to either one of two types of transfer, that of solute from the surface of solids through an interface film and into the surrounding liquid, and that of solute in the capillaries of solids through the capillaries into the surrounding liquid. In the first case of transfer through an interface film, the following basic equation for rate of solution of a solid into a liquid is used:

$$dc/dt = k(c' - c)$$

This equation states that the rate of change or first derivative of solute concentration,  $c$ , in the surrounding liquid with respect to time,  $t$ , is equal to a diffusional coefficient times the difference in concentration between the solid surface and the surrounding solvent. The solute concentration,  $c'$ , in the liquid at the solid surface is taken to be in equilibrium with the solute in the solids. In some cases it has been assumed to be a saturation concentration, and in others proportional to the undissolved solute. In the case of solute adsorption in the solids, a fractional power of the solute concentration at the interface is taken as proportional to the adsorbed solute concentration.

The diffusional coefficient is constant only for specific and limited conditions. It is dependent on the materials involved; the size, shape, and structure of the solids; temperature; liquid viscosities; velocity of liquid flow or agitation; and other conditions of the extraction system.

In general, only by setting up definite conditions on carefully selected materials may the equation be effectively applied, thus determining the relationship of  $c'$ , and making  $k$  constant or of known dependency on controlled variables of the system. Boundary conditions are then determined, and the equation is integrated and put in terms of the operating variables of the equation.

For transfer of solute through capillaries of solids a similar situation exists. The general equation of diffusion used is an expression of Fick's law:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

Here, the rate of change of solute or derivative of solute concentration in the surround-

ing liquid with respect to time is equal to a diffusional coefficient,  $D$ , times the second derivative of the concentration with respect to the distance from the interior to the surface of the porous solids. By careful control of extraction conditions and selection of materials, boundary conditions can be set, the diffusion equation integrated, and the resulting equation expressed in terms of known or determinable operating factors.

Boucher, Brier, and Osburn (4) using carefully prepared porous clay disks of uniform dimensions that were impregnated with soybean oil showed that an integrated form of Fick's law under specially set conditions applied to the extraction of the oil from these disks with chlorinated hydrocarbon solvents. However, application of these methods to the extraction of oil from soybean flakes with such solvents has not been as effective or conclusive.

These and other diffusional methods for determining solute transfer rates have not been very satisfactory. However, they appear to be the most promising means for eventually solving extraction problems involving full immersion or spray percolation methods. For intermittent drainage extraction problems, such diffusional rates should be developed to determine the extent of deviation from ideal equilibrium extraction conditions, unless one wishes to continue depending on experimentally obtained efficiencies to relate the number of equilibrium units to the number of actual extraction units.

### Factors Influencing Extraction Operations

**Materials Involved.** As a carrier of the solute, the solids play an important part in an extraction operation. Their structure and other physical characteristics as modified by preparation for extraction are determining factors in making the solute accessible to solvent action.

Solute at the surface of the solids is most readily removable by the solvent. Therefore subdividing the solids to increase the surface and to expose and bring additional solute to the surface improves extraction. However, reduction of the solids to finer particles has limitations. Too fine a subdivision may result in packing of the solids during extraction and thus prevent free flow of solvent over the surface. Extraction is particularly difficult when the finely divided solids are treated as a stationary, unagitated batch charge or are carried through in continuous extraction as an undisturbed mass. Channeling is bound to occur and much of the surface is not adequately exposed to the moving solvent. Furthermore, an appreciable amount of liquid becomes entrained in the interstices of a mass of fine solids and it becomes difficult to displace this liquid with inflowing liquid.

Dispersion of the particles in the liquid solution by agitation or by vigorous continuous throughflow of liquid permits thorough contacting of the extended surfaces by the moving solvent. Such operations, while giving good extraction, will in some cases result in the suspension of fine particles in the outflowing liquid and may require difficult filtration and clarification methods for separation.

Rather than excessive subdivision, the use of solids having an open porous structure or prepared into sizes and shapes giving large surfaces and an open type of packing for free flow of solvent is the requirement for many extraction methods. For example, in the preparation of oilseed meats, much care is expended in efforts to produce thin, firm flakes without fines for obtaining extended surfaces while still permitting ready flow of solvent through the massed solids.

The bulk density of solids prepared for extraction, together with the time of contact with solvent for the required extraction, sets the weight capacity of most extractor designs. Such is the case for batch-extraction vessels that hold a fixed volume of solids charge for a given extraction time. In continuous operations, usually a fixed volume of solids is carried through the extractor at a given rate of movement or at a set throughput time.

Solvent selection, where there is a choice among nonaqueous solvents, requires careful thought, as many properties of the solvent affect its suitability for obtaining the most effective and economical extraction. The extent and rate of solution of a solute and of impurities in the solids by a solvent will be appreciable factors in determining the size of the extractor, overall operating costs, the cost and type of recovery equipment, and the quality of the products. Sometimes, to avoid subsequent expensive purification operations, a less effective but more selective solvent is chosen over one of higher dissolving power that also dissolves undesired impurities from the solids.

The boiling points of the solvent and of its solutions with the solute normally put limits on the extraction temperature, determine the ease of recovery of the solute from the extract solution and of the extracted solids, and affect the solvent loss of the operations. Generally, the higher the temperature, the more rapid and thorough the extraction. Except where soluble impurities become a problem, extraction is conducted somewhat below but as close as practical to the boiling point of the solvent. When higher than boiling temperatures are necessary for extraction, extractors for pressure operation, of special design and more expensive construction, are required.

The boiling points, heat properties, and vapor pressures of the solvents and their solutions with the solutes determine the type of solvent-vaporization operations normally used for solvent and solute separation and recovery, the cost of such equipment, and whether atmospheric pressure or vacuum should be used for further operation. These properties of the solvent also indicate its suitability for the recovery of solvent-free extracted solids, particularly when valuable, heat-sensitive solids are involved. Immiscibility of the solvent with water, that may be present in the solids for extraction or that results from a steam-stripping operation, also helps fix the ease and means of solvent recovery for re-use in extraction.

Viscosity of the solvent, as a specific property of the liquid, as a function of temperature, and as changed by solution with the solute, influences thoroughness and rate of extraction. Low-viscosity liquids tend to penetrate better into the interstices between solids and into the pores of solids for improved extraction and give increased diffusion rates for solute transfer.

Density of the solvent and its relation to the actual solids density affects design and operation of the extractor. It determines whether upward or downward solvent flow is necessary in extractors of vertical or sloping design, particularly of the full immersion type. In such units, batch or continuous, some claim that downward flow of solvent when density increases with solute concentration, and upward flow when density decreases, is desirable to minimize mixing and dilution of the more concentrated solution due to convection currents. However, thermal differences and other factors that set up undirected liquid movements are believed to be more pronounced in causing undesirable mixing of concentrations and resulting loss in extraction efficiencies.

Solvents used for extraction purposes are volatile to permit ready recovery of the products by vaporization of solvent. With the exception of water, the solvents require

vaportight extraction equipment to minimize solvent loss. Such losses in addition to being costly, especially for expensive solvents, could set up industrial hazards when the solvents are flammable or toxic. Solvent losses, with such costs and hazards, can be kept low, particularly in continuous extraction plants, by use of adequately designed auxiliary equipment. Still, the cost of the solvent, its flammability and toxicity are often the deciding factors in solvent selection.

The corrosive properties of the solvent and its solutions are definite factors in setting equipment costs, particularly where metal construction is required. Selection of the proper material of construction not only insures long life for equipment but avoids loss in product quality and value through contamination or discoloration.

**Operating Variables.** High solute concentrations of outflowing extract liquors are desirable to reduce distillation and recovery costs. To obtain the higher concentrations means additional time or number of units for extraction or a decrease in thoroughness of extraction. From considerations of diffusional rates, increased concentration of the liquid surrounding the solids reduces concentration differences and consequently the solute-transfer rate. Also, from equilibrium considerations, the liquids entrained in the solids have higher solute concentrations and require more steps of liquid contacting and draining to reduce the solute concentrations sufficiently.

The term solvent ratio, as commonly used, means solvent weight flowing into the extractor per unit weight of solids fed into the unit. This solvent weight is the sum of the solvent weight leaving the extractor entrained in the solids and that leaving with the outflowing extract liquid. The entrained solvent is a constant for the operation, depending on the solvent and solids characteristics, and the time and the way of draining the discharged solids. Therefore, increasing the solvent ratio increases the solvent in the extract liquid and reduces its concentration, thus increasing the rate and extent of extraction.

While the effect of high liquid retention in the solids is obvious in decreasing readiness of extraction by intermittent drainage methods, it would be difficult to measure or fully conceive the amount of liquid entrained in the solids for the full immersion and spray percolation methods. Nevertheless, it can be understood that in these two methods there is a holdback of liquid by the solids charge in batch extractions and a carry back of liquid with the moving solids in continuous operations to decrease appreciably the extraction of the solute.

Increasing time of contact between solids and liquid increases the extent of extraction and also the size of the extractor, although in intermittent drainage extraction the number of periodic drainages accomplished on the solids can be more important than the total contact time. The countercurrent flow in multibatch and continuous operations is essential for thorough extraction of the solids and for good concentrations of outflowing extract liquids. A long path of solvent travel is needed to get sufficient time of contact and good countercurrent flow. This length is obtained in multibatch extraction by the flow of solvent consecutively through a number of charges, this number times the depth of the charge giving the total distance of solvent travel. In continuous extraction, the designs are all toward giving long paths of travel for both solids and the counterflowing liquid.

Slow turning of the solids has been found helpful in extraction to expose all the surfaces of the particles to liquid flow, to break up liquid channels in the solids, and to reduce liquid entrainment in the solids. Such slow stirring of solids has been effec-



tively employed in both batch and continuous extractors for breaking up and turning over the solids masses.

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FRANK LERMAN

### LIQUID-LIQUID EXTRACTION

Liquid-liquid extraction or, more briefly, liquid extraction refers to the transfer of one or more components between two liquid phases. Its purpose is to purify one or more compounds or to effect a more economical recovery of a component than is possible by other means. The process in which a component is removed from one solvent by contacting with another immiscible solvent is called *simple liquid extraction* and is the oldest type of liquid extraction. In the laboratory the process is generally carried out in a separatory funnel by successive extractions of the one solution with fresh portions of the other solvent. A single extraction removes part of the component but a fraction always remains in the original solution. Thus a number of such treatments are necessary to extract a high percentage of the component. This technique requires excessive quantities of solvent, and in plant operation it is generally carried out by a countercurrent technique which can give the maximum amount of extraction with a given quantity of solvent.

It is also possible to separate a mixture of two or more components by their unequal distribution between two liquid phases. This process is called *fractional liquid extraction* because of the analogy with fractional distillation. In general, one solvent will have a preferential dissolving power for one component and the other solvent for the other components, and by successive distribution of the mixture between the two solvents it will be possible to separate the mixture. However, in most cases the difference in the equilibrium conditions is small and a large number of contacts are required to effect a good separation. The process was first considered on a batchwise laboratory scale in 1925 and rejected as impractical (13). However, Craig developed an apparatus for conveniently carrying out the multiple operations of the batchwise extraction process (10,11). The apparatus was especially suitable for microchemical studies and could be used to ascertain the purity of a compound and to detect mixtures by comparing the distribution curve obtained for a large number of such extractions with the theoretical curve. This device was primarily designed to determine distribution data and could not be used to give an appreciable yield of purified product.

It has only been in the last few years that sufficiently efficient equipment has been

available for carrying out the continuous fractional liquid extraction in a single laboratory column (25). With this column it is possible to obtain products that have been subjected to sharp fractionation between two solvents. The previous applications had been limited to easy fractionations requiring relatively few stages.

The theory of the design of extraction equipment has much in common with the theory of distillation equipment, and reference will be frequently made to the article *Distillation*, and also to *Absorption*.

#### INTERPRETATION OF LIQUID-DISTRIBUTION DATA

The design of liquid-liquid extraction operations depends upon a knowledge of the distribution or relative solubility of a solute between two solvents that are not completely miscible. Several methods have been developed for studying these data

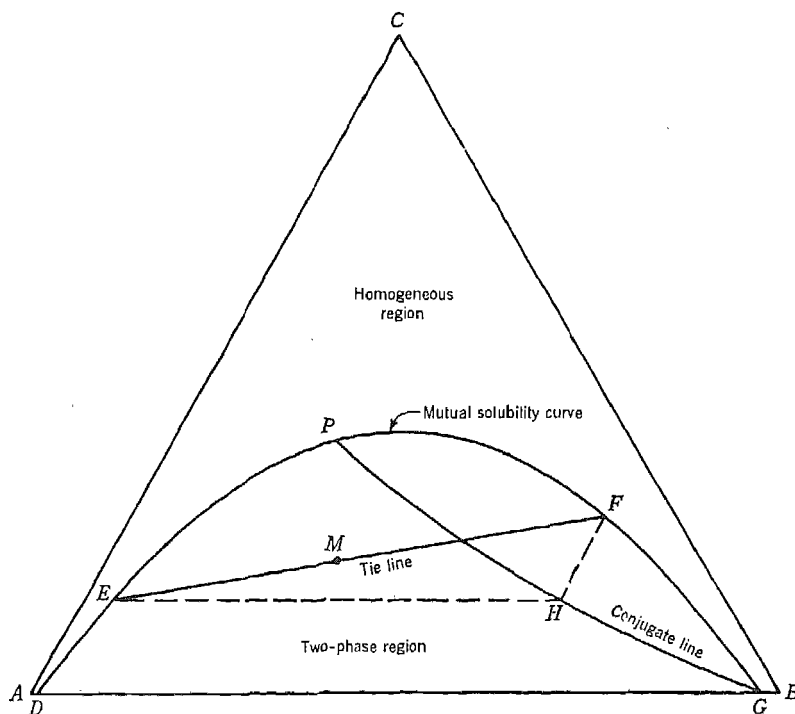


Fig. 1. Ternary diagram showing mutual solubility curve and conjugate line.

(12,29). In the ternary diagram (see Fig. 1), the corners A and B represent solvents, and C a third substance, in this case miscible with A and B. The curve *DEPFG* represents the mutual solubility curve and any composition lying inside this envelope will separate into two liquid phases. This is called the heterogeneous region and a mixture of composition *M* will separate into two phases of compositions *E* and *F*. The line connecting these two compositions which are in equilibrium with each other is called the tie line. Compositions outside of the mutual solubility curve are in the homogeneous region and do not separate into two phases.

It will be observed from Figure 1 that it is difficult to interpolate between the tie lines on this type of diagram and several methods have been developed for accomplishing this interpolation with better accuracy. One method consists of constructing the

"conjugate" line (or curve) by laying off  $EH$  parallel to side  $AB$  of the ternary diagram and line  $HP$  parallel to side  $AC$ . The intersection,  $H$ , of these two lines defines the conjugate curve  $GHP$  from which any tie line can be found by reversing the construction just described. The conjugate curve intersects the mutual solubility curve at the point  $P$ , known as the "plait point." At this point the two phases in equilibrium are identical and it may be considered as a limiting condition for extraction. Other methods for constructing the conjugate line have been described; this line allows an extrapolation to the plait point as well as facilitating interpolation of the data.

Another method for accomplishing the same result is to plot the equilibrium conditions as the concentration of the solute in one phase against the concentration in the other phase. This is the most popular type of graph and will be discussed later in its application to design calculations. The plait point on this plot is the intersection of the equilibrium curve with the  $45^\circ$  or  $y = x$  line as shown in Figure 5.

Other methods for plotting tie-line data have been proposed. All of these may be conveniently extrapolated to determine the plait point, but it should be noted that slightly different points may be obtained by the different methods depending upon the extent of the extrapolation required. This is of minor significance because in the extraction operation it is undesirable to approach very close to the plait point due to the high mutual solubility of the solvents in this region.

*Correlation of Tie-Line Data.* Brancker, Hunter, and Nash developed an empirical scale on which the tie-line data for a large number of systems investigated gave straight lines (5). Campbell suggested plotting the logarithm of the concentration in one phase against the logarithm of the concentration in the other phase to obtain a straight line (6). Bachman derived the algebraic expression for the Brancker, Hunter, and Nash plot and demonstrated its application without the use of the empirical scale (2); and Othmer and Tobias showed that for the case of immiscible solvents which were used in the previous correlations the two constants in the equation of Bachman were related (20). They introduced a second constant by plotting the functions on logarithmic scales; the second constant was the slope of the lines, while the intercept was related to the original constants of Bachman. This method indicated broader application, but the empirical nature of the method led to results inconsistent with some subsequent data.

The previous empirical methods of correlation required some actual liquid data in order to determine the complete equilibrium curve. Recently the interest in this field has been in the prediction of liquid distribution data from other available equilibrium data. These latter methods are based on mole fractions; the weight fractions used in all the previous empirical methods have been discarded in favor of mole fractions. All subsequent discussion here will be in terms of mole fractions.

The simplest method for the prediction of liquid-distribution data from vapor-liquid equilibrium data is that of Hildebrand (16). This method neglects the partial miscibility of the solvents and is based on the principle that two liquid solutions in equilibrium with the same vapor must be in equilibrium with each other. Thus, if the partial pressures of the solute from the solutions with each solvent are known, the liquid-distribution data can be determined as the two concentrations giving the same partial pressure of the solute.

The first attempt to predict liquid-distribution data by taking into account the partial miscibility of the solvents was described by Othmer and Tobias (20). They assumed the partial pressure or activity to vary linearly on a ternary diagram at a constant solute concentration between the known values in the two pure solvents. They used weight fractions in the ternary diagram and interpolated on this basis. Colburn and Schoenborn interpolated on a mole basis assuming that the logarithm of the activity varied linearly between the two terminal values at a constant solute concentration (9). Treybal reviewed the methods for predicting the distribution data and suggested a new method based on "effective concentrations," which in effect used two separate curves for the interpolation, but over the range of concentrations where each was used, it more nearly resembled the variation observed from actual data (30). Scheibel and Friedland proposed a graphical empirical method for obtaining a smooth curve between the two terminal values, which resembled the actual variation (27). They demonstrated its application in predicting ternary vapor-liquid equilibria on nine systems

reported in the literature, most of which could not be estimated by previous methods. It was also applied with excellent results to the prediction of five sets of distribution data available in the literature. The accuracy of the method in many cases is limited by the reliability of the binary vapor-liquid equilibrium data.

Algebraic methods for predicting the variation of the activity coefficients in ternary systems by means of thermodynamically consistent equations have been described under *Distillation*. These could also be used to estimate activities along the mutual solubility curve so that the distribution data may be properly estimated by taking into account the mutual solubility of the solvents.

These previous methods have been considered as applied to the distribution data for one solute between two solvents and are thus applicable to simple extraction operations. The same basic principles have been applied to the calculation of liquid-distribution data for two or more components between two solvents for the study of fractional liquid-extraction operations, and methods have been suggested for correcting the activity coefficients for the presence of both solutes in each solvent. This will be described subsequently as applied specifically to fractional liquid extraction. The interpretation and correlation of distribution data for fractional liquid-extraction operations with external reflux will be discussed under this heading because of their specific applications to this type of operation.

### Simple Liquid Extraction

In simple liquid extraction a component is transferred from one solution into another solution. There may be one or several advantages in transferring a compound into the other solution. Starting, for instance, with a dilute and heavily contaminated aqueous solution of a compound less volatile than water, liquid-liquid extraction with an immiscible organic solvent may lead to a concentrated and highly purified solution (raffinate) of a valuable material. The advantages are obvious. Concentrating a dilute and contaminated aqueous solution by straight evaporation is costly, leads to an impure concentrate, and may be accompanied by a considerable destruction of the product. Concentration after liquid-liquid extraction with an organic solvent is comparatively cheap, leads to a refined product, and avoids destruction.

In some cases the component extracted may be more easily separated from the second solution than from the original solution; this application has many ramifications. It may be used to extract a component from a solvent with which it forms an azeotrope into a solvent with which it does not form an azeotrope. A large-scale commercial application of this type of extraction is the removal of a component present at a dilute concentration in a lower-boiling solvent by extraction with a higher-boiling immiscible solvent. This effects a substantial saving of heat because it is necessary only to distill off the smaller quantity of the component from the final extract solution as compared to distilling off the larger amount of original solvent. It has been extensively applied to the recovery of acetic acid from dilute aqueous solutions; the higher-boiling ketones have been found to be especially suitable for this extraction (35-37).

### MULTIPLE CONTACT WITH FRESH SOLVENT

The laboratory technique for simple liquid extraction consists of providing contact between the solvent and the solution to be extracted by shaking vigorously in a separatory funnel and then separating the layers. This operation is represented graphically in Figure 2. Assuming that the solvents are completely immiscible and that equilibrium between the two solutions is attained, the concentrations of the two phases correspond to a point on the equilibrium curve. Thus, if  $H$  moles of a heavy solvent containing a solute at a concentration of  $x_0$  moles per mole of solvent is mixed with  $L$

moles of a light solvent and the mixture shaken up to obtain equilibrium, the final concentrations may be assumed to be given by the point  $(x_1, y_1)$  on the equilibrium curve. This point can be located by considering a material balance on the two phases such that:

$$y_1/(x_0 - x) = H/L \quad (1)$$

The left-hand side of this equation can be seen to be the slope of the line between  $(x_0, 0)$  and  $(x_1, y_1)$  in Figure 2 considered in the negative direction. The calculation can be repeated as shown by constructing lines of slopes  $-H/L$  through the raffinate concentrations to the equilibrium curve for successive treatments of the raffinate with the same quantity of fresh solvent.

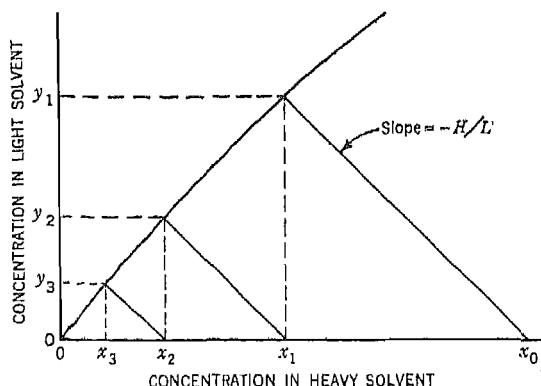


Fig. 2. Graphical solution of multiple batchwise liquid extraction with fresh solvent.

For the case of systems obeying the ideal distribution law, so that the concentration in one phase is always proportional to the concentration in the other, the equation of the equilibrium curve is:  $y = Dx$ . It has been shown by Underwood that the relationship between the initial and final concentration in the raffinate after  $n$  extractions is (32):

$$x_n = \frac{x_0}{((LD/H) + 1)^n} \quad (2)$$

where  $x_n$  = final raffinate concentration after  $n$  extractions. This equation has been represented graphically (32) and nomographically (14). From equation (2) it is also possible to determine the number of extractions with a given ratio of solvents, necessary to reduce the raffinate concentration to any desired amount. Thus:

$$n = \frac{\log (x_n/x_0)}{\log \frac{1}{1 + (LD/H)}} \quad (3)$$

In the use of partially miscible solvents, account must be taken of the dissolved solvent in each of the phases. The calculations are carried out on a ternary diagram as shown in Figure 3 (12,29). The feed composition is represented by the point  $F$ . The point  $S_0$  at the solvent corner of the diagram represents the fresh solvent and coincides with the corner only when the solvent contains none of the other constituents in the

feed. The compositions of all mixtures of the feed and the fresh solvent lie along the line  $S_0F$ ; the location depends upon the relative amounts of each in the mixture. Thus the first mix point  $M_1$  is located so that the ratio of the distance  $M_1F$  to  $S_1M_1$  is equal to the ratio of the solvent to the feed quantity in the same units of the ternary diagram. The mixture  $M_1$  must fall in the immiscible region and will then separate into two phases given by the tie line through this point.

The extract composition from the first extraction is designated by  $S_1$  at the solvent end of the tie line, and the raffinate composition is designated  $R_1$  at the opposite end. The raffinate  $R_1$  is mixed with fresh solvent and the mix point  $M_2$  is located as before,

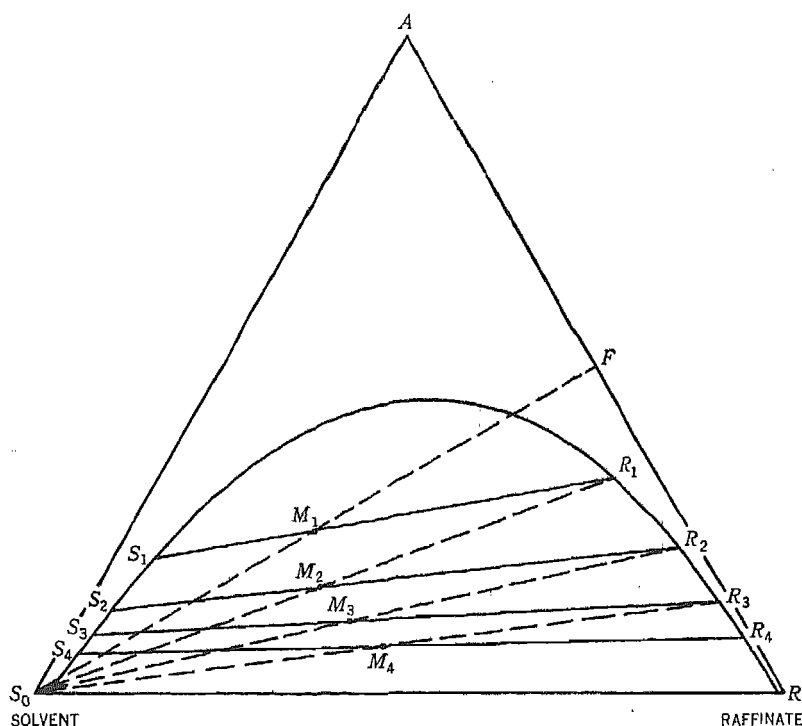


Fig. 3. Equilibrium-stage calculation on a ternary diagram for multiple, batchwise extraction with fresh solvent.

and the equilibrium-stage calculations are continued, as shown, until the desired raffinate concentration is obtained. It has been previously mentioned that interpolation of the tie lines on a ternary diagram cannot readily be made by inspection; reference to the conjugate line, or to a separate equilibrium curve as shown in Figure 5, will give a more reliable interpolation. The location of the proper tie line through the mix point is by "cut and try" regardless of which method is used to represent the tie-line data.

#### CONTINUOUS COUNTERCURRENT EXTRACTION

Because of the economic advantages of continuous countercurrent extraction this type of operation is preferable for plant-scale operations. In the case of completely immiscible solvents and ideal distribution (so that the concentrations in the two solvents are proportional), it can be shown by material balances and equilibrium con-

ditions that when the fresh solvent contains no solute, the relationship between the solute concentrations in the feed and final raffinate solution is given by:

$$x_n = \frac{(LD/H) - 1}{(LD/H)^{n+1} - 1} x_0 \quad (4)$$

where  $x_0$  = solute concentration in feed;  $x_n$  = solute concentration in raffinate after  $n$  equilibrium stages;  $L$  = flow rate of light solvent;  $H$  = flow rate of heavy solvent; and  $D$  = distribution coefficient. Underwood has presented a chart by which the unextracted fraction,  $x_n/x_0$ , may be determined directly from the values of  $LD/H$  and the number of equilibrium stages,  $n$ , or any of these values may be determined from the other two (32).

In general, however, the distribution coefficient,  $D$ , will vary with concentration, even though the solvents are almost completely immiscible. A completely rigorous

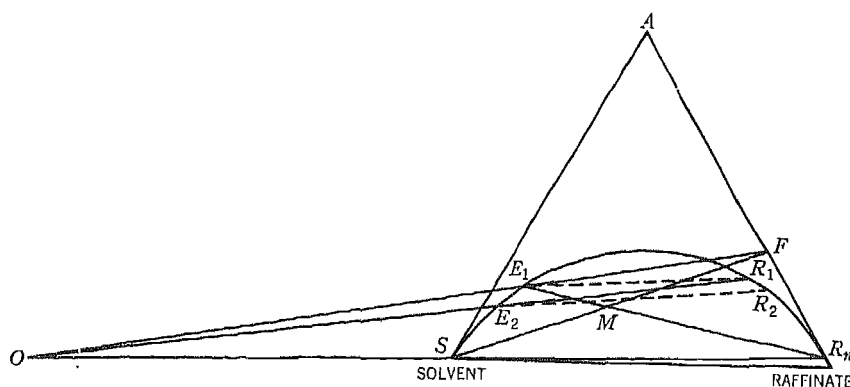


Fig. 4. Graphical stage calculations for countercurrent liquid extraction by the method of Hunter and Nash.

method for calculating the number of equilibrium stages, taking into account the partial miscibility of the solvents as well as varying distribution coefficient, was developed by Hunter and Nash (17) and is illustrated in Figure 4. A feed composition  $F$  is to be extracted with solvent in a countercurrent operation to produce a raffinate of composition  $R_n$ . From the flow rates of the solvent and feed the mix point  $M$  is located along line  $SF$ . The mix point represents the total material introduced into the column and must also represent the total material leaving the column. It therefore lies on the line between the raffinate composition  $R_n$  and the extract composition  $E_1$ . Projection of a line through  $R_n$  and the mix point  $M$  to the mutual solubility curve gives the final extract composition  $E_1$ . The relative rates of the raffinate and extract are given by the distances  $E_1M$  and  $MR_n$ . The raffinate solution from the first stage can be located by the tie line through the point  $E_1$ ; this is shown at point  $R_1$ . It can also be shown by rearranging the overall material balance that the difference between the extract and feed must be the same as the difference between the solvent and raffinate. The point that satisfies this condition lies on the intersection of lines  $FE_1$  and  $R_nS$  and is shown at point  $O$ . It can also be shown from a material balance that the difference between the two streams at any point in the column is the same as at the ends. Thus the line through these compositions must also pass through the point  $O$ . Accordingly, the line

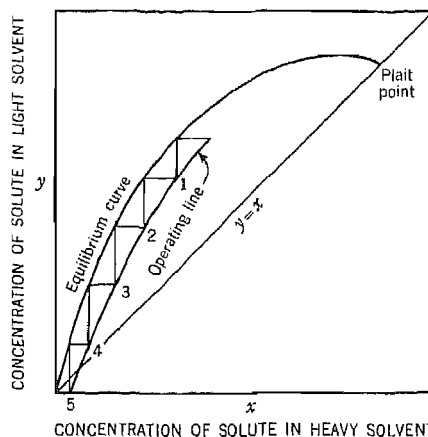
between  $R_1$  and  $O$  in Figure 4 intersects the mutual solubility curve at concentration  $E_2$ , which is the solvent composition leaving the second theoretical stage. This construction is equivalent to a graphical material balance. The tie line through the point  $E_2$  locates the point  $R_2$  and this is equivalent to a graphical equilibrium calculation. Thus by alternate material-balance and equilibrium calculations the procedure can be repeated until the desired raffinate composition is obtained.

In a similar manner the calculations may be carried out in a reverse order starting at the point  $R_n$ . However, the first method is preferable because it immediately shows with the first equilibrium calculation whether the solvent rate used is above the minimum. If the first tie line is above the line  $E_1F$ , it is apparent that the raffinate composition cannot be realized and the solvent rate is below a definite minimum. When the tie line coincides with the line  $E_1F$ , the solvent rate is a minimum value which would require infinite stages. Any solvent rate above this will give the desired separation in a finite number of stages and therefore represents a practical separation.

Varteressian and Fenske modified the method of Hunter and Nash to eliminate the use of the tie line on the ternary diagram (33). They located the operating line on any  $xy$  diagram, as shown in Figure 5, by the intersections of the lines in Figure 4 passing through point  $O$  with the mutual solubility curve, and plotted the concentration in the solvent phase against the concentration in the raffinate phase. These concentrations may be in mole or weight fractions as read directly from the ternary diagram or may be converted to any other basis. However, due to the mutual solubility of the solvents, the operating line will not be straight by any method of expressing the concentrations; therefore the most convenient Figure 5 the tie-line data are plotted to locate the number of stages required are stepped off between the absorption calculations. This is equivalent to the balance calculations and is mathematically identical to Nash, but it is somewhat more convenient than the  $x/y$  plot of Figure 5.

In the case of countercurrent extraction in a packed column the concentrations vary continuously, and if the equilibrium curve and the operating line have appreciably different slopes, the "equilibrium stage" (or the equivalent "theoretical stage," as is generally used in this case since actual physical stages do not exist) is not a good criterion for design. In this case the transfer unit proposed by Chilton and Colburn is a better measure of the difficulty of separation because it is based on an integrated driving force in preference to a constant driving force over the theoretical stage (7). For the technique for determining the proper mean driving force between the equilibrium curve and the operating line see *Absorption*.

Liquid extraction has been applied to the refining of lubricating oil. The crude oil is a mixture of a large number of compounds, some desirable, some undesirable



**Fig. 5. Graphical stage calculations by the method of Varteressian and Fenske.**



The exact concentration of each component in the mixture cannot be determined, and it would be exceedingly tedious to make the necessary equilibrium-stage calculations with this information if it were available. An empirical method for expressing the concentration of undesirable constituents has been developed based on the viscosity-gravity constant (VGC) (12). This constant is an additive function of the mixture, so that if the desired raffinate has a VGC of 0.80 and the extracted oil has a VGC of 0.90, a mixture of equal parts by volume of each oil would have a VGC of 0.85 and be located half-way between the two products. This satisfies the conditions of the ternary diagram so that the one side may be calibrated from 0.80 to 0.90 to represent the composition of the solvent-free oil mixture. The opposite vertex of the triangle represents the pure solvent and the equilibrium-stage calculations may then be carried out as previously described. Rushton has used a slight modification of this method and demonstrated its application in the refining of lubricating oil with nitrobenzene solvent (24). However, all oil stocks that must be refined are different, and the equilibrium and solubility data would have to be determined for all the individual feed stocks; thus this method has not had very wide application. It is common practice to process the crude oil through a pilot plant to determine the yield and operating conditions because this is simpler than determining all the necessary equilibrium and solubility data, and it provides at the same time the necessary performance data, so that the product yields can be safely guaranteed on the commercial design.

### Fractional Liquid Extraction

By simple liquid extraction it is possible to remove a component from one solution into a second solvent. However, if another component that is more soluble in the first solvent is present in the second solvent, this component would be simultaneously transferred in the opposite direction at the same solvent rates. Thus, by introducing a mixture of two components into the middle of a column in which two solvents are flowing countercurrently, it is possible to achieve a separation, because, at the proper rates, the respective components would be removed with the solvent in which each was relatively more soluble. With sufficient stages, a substantially complete separation is possible. Any liquid extraction in which two components can be separated from each other may be defined as fractional liquid extraction.

#### FRACTIONAL LIQUID EXTRACTION WITH SINGLE SOLVENT

It is sometimes possible to separate a binary mixture completely into pure components if both of these components are only partially soluble in the solvent. It is then possible to return some of the product removed with the solvent to the column instead of employing an additional foreign solvent. This is a special type of operation called fractional liquid extraction with external reflux and is shown in Figure 6 as applied to the separation of methylcyclohexane (MCH) and *n*-heptane, using aniline as the solvent (37). The MCH is returned to the bottom of the column as "reflux," accomplishing the same effect as reboiler vapor at the bottom of the distilling column. This MCH phase passes upward through the column countercurrent to the aniline, which is introduced at the top of the column. As it passes upward through the column, it dissolves in the aniline and simultaneously extracts or displaces the *n*-heptane from the aniline solution, so that at the top of the column the hydrocarbon phase consists essentially of *n*-heptane. At the top of the column, the aniline entering becomes

saturated by dissolving the proper amount of the *n*-heptane, and the excess passes overhead as the *n*-heptane product. The dissolved hydrocarbon acts as the reflux in the conventional distilling column, although at this end of the column it is actually an internal reflux resulting from the introduction of the solvent. At the other end of the column, the MCH return to the column may be considered as an external reflux stream.

Two other methods have been used to produce this reflux in the extraction column. These should be more clearly defined as fractional liquid extraction with internal reflux. One method is to change the temperature of the solvent at the discharge end and thus precipitate out the necessary reflux, which then flows back through the column, countercurrent to the solvent to the other end, where it is dissolved in the incoming fresh solvent and is thus recycled. Another method is to add to the solvent discharge end of the column a second solvent which is soluble in the first solvent but immiscible with the product being removed at this end of the column, so that some of the product will be precipitated from the solvent and return through the column countercurrent to the first solvent. This is distinguished from the general case of two solvents, in that the second solvent does not pass countercurrently through the column against the first solvent, but is completely soluble in the first solvent and is immediately eliminated at the same end along with this solvent. The product precipitated from the solution provides the necessary reflux to the column.

Maloney and Schubert developed a method for carrying out these graphical calculations for fractional liquid extraction with a single solvent based on the Ponchon principle which is well known in distillation (18).

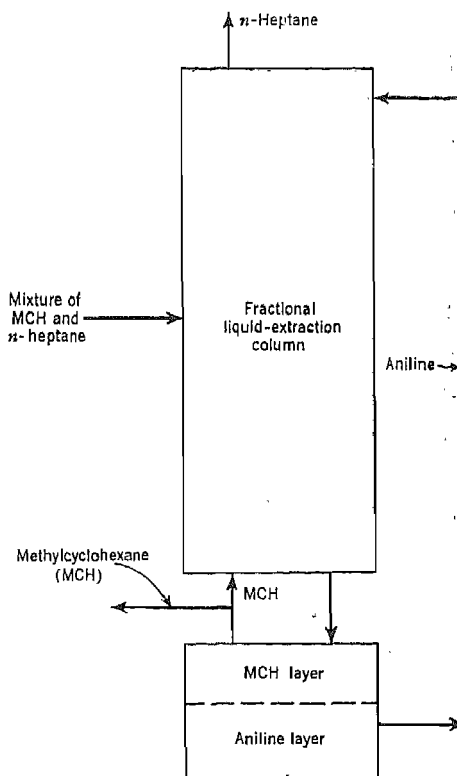


Fig. 6. Schematic diagram of fractional liquid-extraction process with external reflux.

#### FRACTIONAL LIQUID EXTRACTION WITH TWO SOLVENTS

This operation is a more general case because both components of the mixture may be completely miscible with both solvents in all proportions. Therefore, in contrast to the previous case, there is no limitation on miscibility of the components with the solvents, and any conceivable mixture may be separated by this method. The only requirement is that the two solvents be immiscible in each other. This is a physical requirement for operation of the process. It imposes no excessive restrictions on the solvents because only dissimilar solvents will have a selective effect on the components of the original mixture, and all solvents which are immiscible in each other are appreciably dissimilar.

The first consideration of this process on the basis of individual batchwise counter-

current operation led to the conclusion that it was impractical when the relative distribution was small because a large number of contacts would be required for a good separation. Craig developed a relatively simple device for carrying out twenty or more countercurrent extractions simultaneously and improved the yield to make the process practical on a laboratory scale (10,11). The unit was designed primarily for microchemical work on biologically active compounds. However, the yield was far from complete and it could not be used for large-scale operations. It was useful in determining liquid-distribution data and in testing the homogeneity of small amounts of material. In order to be carried out on a commercial scale, this process requires an efficient type of continuous countercurrent in which a large number of theoretical stages can be obtained in a single compact unit, as is done in a distilling column; such a unit will be subsequently discussed (see p. 136).

The separation of components by fractional liquid extraction between two solvents depends upon the different solubility of the components of a mixture in different solvents. The best criterion for solubility is the activity coefficient (an inverse measure of solubility). At the higher values, the compounds are only partially soluble; lower values give a measure of the dissolving tendency. The methods for predicting the distribution coefficients for any component between two solvents have been previously described. A comparison of the distribution coefficients of two components between the same solvents will show the effectiveness of these solvents in separating a mixture of these components. The ratio of these coefficients is called the relative distribution, and, in the case of ideal systems, it could be used to calculate equilibrium curves on a solvent-free basis.

The choice of the solvents for a separation by fractional liquid extraction will be possible by consideration of the same generalizations described under *Distillation* for choosing the solvents for extractive distillation. The mechanism of the separation depends upon the same principles, namely, the difference in the deviations from ideality of the two components in a solvent. In the liquid-extraction process, it is possible to choose two solvents so that the effect of each solvent will be additive. Thus, liquid extraction can give a greater relative distribution than extractive distillation, which depends upon only one solvent.

By the application of the same generalizations, it is also possible to predict distribution coefficients quantitatively when the activity coefficients for the component in a particular solution are unknown. These generalizations are as follows: (1) The activity-coefficient curve of a component in any solvent is very nearly the same as in close homologs of this solvent. (2) The activity-coefficient curve of any component in a solvent is very nearly the same as that of its close homologs in the same solvent. (3) When components are ideal with each other, their activity coefficients from a solvent are the same as when each component is present in the solvent at their combined concentration; or in other words, their activity coefficients are independent of their relative amounts present in the solution and are functions of the solvent concentration only.

These assumptions have been used to predict distribution coefficients for several systems, and the results were successfully used to correlate performance data on a liquid-extraction column (25,26). The calculations were based on the previous method of Hildebrand (16) by neglecting the mutual solubility of the solvents, and wherever possible, correcting the activity coefficients in each solvent for the effect of all the other components present. This latter correction was made by calculating the

ternary coefficients from the binary data by the method of Redlich and Kister (23). Figure 7 shows the calculated distribution coefficients for ethyl alcohol and isopropyl alcohol between water and xylene at different concentrations (25).

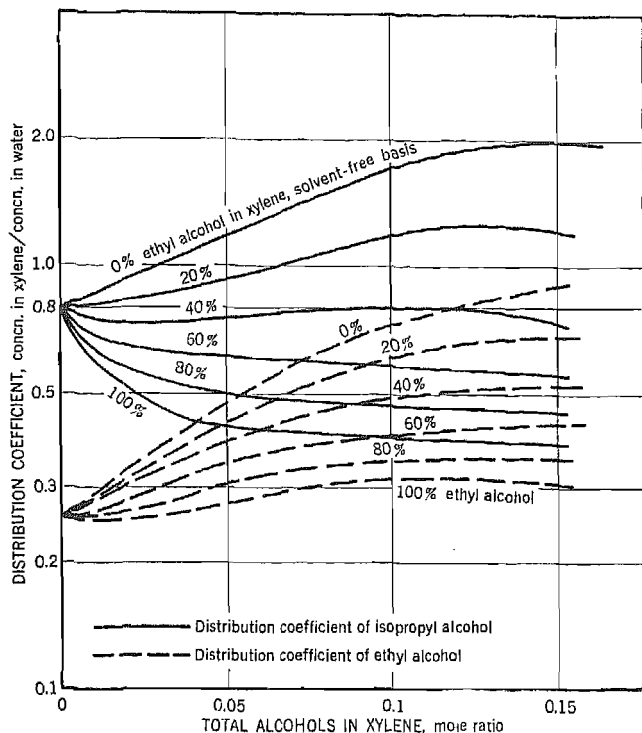


Fig. 7. Distribution coefficients of ethyl alcohol and isopropyl alcohol between xylene and water on a mole-ratio basis (25).

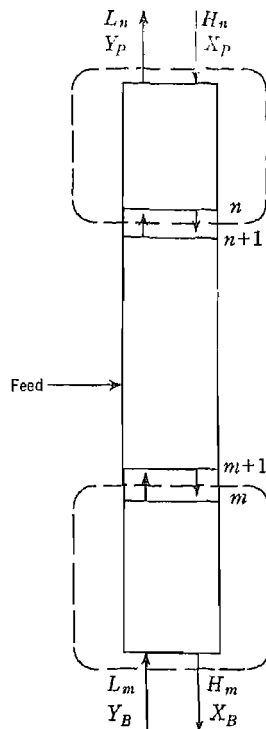


Fig. 8. Material balance and equilibrium conditions (25).

The equilibrium-stage calculations can be carried out from Figure 7 by the following equation, which can be derived from the material balance and equilibrium conditions for any stage above the feed stage, as shown in Figure 8. This equation neglects the mutual solubility of the solvents.

$$Y_{n+1} = (H_n/L_n D_n) Y_n + Y_p \quad (5)$$

where  $Y_{n+1}$  = concentration of a component in light solvent from the  $n+1$ th stage below the top;  $Y_n$  = concentration of component in light solvent from the  $n$ th stage below the top;  $Y_p$  = concentration of component in light solvent leaving the top of the column;  $L_n$  = flow rate of light solvent above the feed;  $H_n$  = flow rate of heavy solvent above the feed; and  $D_n$  = distribution coefficient of component at  $n$ th stage below the top.

Similarly the equation for any stage below the feed can be derived by the same method:

$$X_{m+1} = (L_m D_m / H_m) X_m + X_B \quad (6)$$

where  $X_{m+1}$  = concentration of a component in heavy solvent from the  $m+1$ th stage

above the bottom;  $X_m$  = concentration of component in heavy solvent from the  $m$ th stage above the bottom;  $X_B$  = concentration of component in heavy solvent from the bottom of column;  $L_m$  = flow rate of light solvent below feed;  $H_m$  = flow rate of heavy solvent below feed; and  $D_m$  = distribution coefficient of component at  $m$ th stage above bottom.

In equations (5) and (6), the concentrations are expressed as mole, weight, or volume quantities per unit quantity of solvent. The  $L$  and  $H$  terms must then be in terms of the same unit quantity of solvent. Since the distribution coefficients are most conveniently calculated in terms of mole ratios, these are the usual units. By neglecting the mutual solubility of the solvents, the quantities  $L_n$  and  $H_n$  are constant above the feed, and the quantities  $L_m$  and  $H_m$  are constant below the feed. If no solvent is introduced with the feed, the respective quantities are equal in both sections of the column.

By the application of these equations and the data of Figure 7, it is possible to calculate the variation of the concentration of both components above and below the feed. The point in the column where these quantities above and below the feed are identical for both components is the feed stage. This point can be located by inspection of a plot of the concentration of each component against stage number.

The application of the equations to ideal systems in which the distribution coefficients are constant can be readily observed by noting that  $H_n/L_n D_n$  and  $L_m D_m/H_m$  are constant; the concentration on any tray can be directly calculated from equation (4).

The application of these equations may be modified to apply most conveniently to individual cases. Several such applications have been described (25,26).

### Performance of Liquid-Extraction Equipment

The equipment used for liquid-extraction operations may consist of individual mixing and separating units or it may consist of a column through which the solutions pass continuously and countercurrently.

Various types of mixers have been employed, the most popular of which are mechanical agitators and pumps (see *Mixing*). In the Duo-Sol process for refining lubricating oils the necessary mixing is obtained by pumping through nozzles in the settling chambers (15). The capacities of these plants range as high as 10,000 bbl. per day, making it one of the largest industrial applications of liquid extraction. The use of individual mixing and separating units provides a constant and reproducible performance, because two phases are retained in the mixing unit sufficiently long to come to substantial equilibrium, and the previous method of equilibrium-stage calculations follows exactly the pattern of the actual operations, so the theoretical result can be attained.

The columns used for liquid extraction consist of packed columns, spray columns, baffled columns, and perforated-plate columns. The conventional bubble-plate column employed so widely for distillation operations has such a low efficiency in liquid extraction that it is rarely used. Some attempts have been made to improve the performance of the bubble-plate columns by introducing modifications.

The packed column has received considerable attention as a countercurrent liquid-extraction device and is used in many large-scale applications. The packing is the same as employed in absorption columns and described under *Absorption*. Redistribu-

tion of the dispersed liquid has also been found advantageous, particularly in the large-diameter columns. In packed columns, the solvents flow countercurrently, and the performance is expressed as the height required for the concentrations of the solute to change by the same amount as in the equilibrium stage previously considered. This height is called the "height equivalent to a theoretical stage" and is abbreviated H.E.T.S. It has been evaluated for several systems and for different types of packing in different-size towers. No correlation of the available data is possible at the present time, and the heights generally vary between 2 and 100 ft., depending upon packing properties, column diameter, throughput, and liquid properties.

It was previously pointed out that in the case of packed columns, the transfer unit is a more fundamental method of design than the theoretical stage. However, unlike the theoretical stage, the number of transfer units in a system depends on the solvent concentrations upon which the transfer units are based. When the equilibrium curve and the operating line are parallel, the number of transfer units is the same based on the concentrations in either solvent, and also the same as the number of theoretical stages. However, when the slopes of the equilibrium curve and the operating line differ appreciably, the transfer units are greater, based on concentrations in one of the solvents as compared with the other, and the number of equilibrium stages is intermediate between the two numbers of transfer units. This can be readily seen from the data summarized by Elgin on the extraction of acetic acid from water with isopropyl ether in a spray column (12). Calculated from the same performance data on one run, the H.T.U. (height of a transfer unit) based on water concentrations was 12.8 ft., the H.T.U. based on ether concentrations was 0.98 ft., and the H.E.T.S. was 3.1 ft. Thus, it is apparent that, in comparing the performance data on different columns, this factor must be considered, and it is essential that the H.T.U. be calculated on the same basis. A compilation of considerable other data on liquid-extraction equipment, such as packed columns and spray columns, is also given by Elgin (12). But as yet, the factors involved in liquid-liquid extraction have not been correlated, so that it is not possible to predict the performance of such equipment. Also, the indications in many cases have been that a large fraction of the extraction occurred in the distributing device through which the dispersed solvent was introduced. In these cases, increasing the height of the column will not give a proportionate increase in the extraction efficiency, and care must be taken to properly evaluate the performance before designing a column of greater height for a more difficult extraction.

Spray columns are void or unpacked columns, and the one liquid is introduced through a nozzle which disperses it into small droplets that rise through the other liquid if the dispersed liquid is lighter, or fall through the other liquid if the dispersed liquid is heavier. It has been found that the capacities of these spray columns are increased by providing an enlarged funnel-type end with the spray nozzle located at the widest part (12). Considerable data have been obtained on smaller-size spray columns, but not very many large-scale industrial installations have been made.

Baffle-plate columns contain horizontal plates extending over the major portion of the column, and staggered, so that the liquid in passing through the column follows a long tortuous path back and forth and countercurrent to the other liquid. A lip is provided on the baffle to retain a well of liquid on either the top or bottom of the baffle, depending upon which liquid is the continuous phase in the column. Large installations, in excess of 13 ft. in diameter, have been made with this type of liquid-extraction column, but as yet no performance data have been published on the units.

Perforated plates have also been used to increase the contact between the phases. The design and flow through the unit is similar to the perforated-plate and the bubble-plate columns used in distillation. In one case, a study on a perforated-plate column has indicated plate efficiencies of the order of 5% (19), and in other cases extrapolating the performance data to practical operating conditions indicated plate efficiencies of less than 1% for a perforated plate and an H.E.T.P. (height equivalent to a theoretical plate) of about 50–60 ft. at these operating conditions (31). These practical operating conditions would be based on high recovery at a solvent rate of 20–50% above the minimum. Thus, it may be observed that in some extraction operations 50–100 ft. may be required for one equilibrium stage, and in such cases, the batchwise operation in a series of mixers and settlers is preferable to column operation. Most large-scale extraction processes have been carried out in this batch type of equipment.

In such applications, it is not practical to consider ten or more stages; the usual number is three to seven actual stages.

An effective liquid-liquid extraction device has been developed by Podbielniak, Inc., in which the liquids pass countercurrently through a spiral passageway in a rotor operating at high speed. The heavy liquid moves outward and the light liquid moves toward the center. By regulating the speed of rotation it is possible to exert a separating force several times that of gravity. Solvents may be handled in this unit which emulsify and do not separate by the force of gravity in the ordinary columns. This apparatus has found extensive application in the extraction of penicillin and streptomycin. It has been reported to have 4–7 equilibrium stages on various applications and this is satisfactory for most simple extraction operations. Fractional liquid extraction generally requires a greater number of stages and a series of such units would be necessary for this operation.

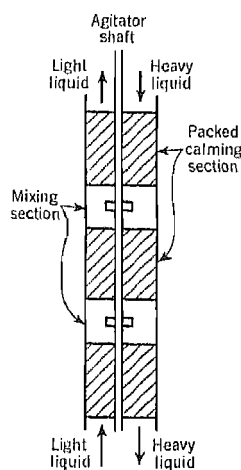


Fig. 9. Schematic diagram of liquid-extraction column (25).

Recently a new type of liquid-extraction column has been described which consists of alternate mixing and settling sections in a single column as shown in Figure 9 (25). The mixing is obtained by an internal rotating stirrer, and the calming section is packed with a loosely woven wire mesh, which acts as an entrainment separator for the dispersed liquid. The data on a 1-in. column of this design indicated that it was possible to obtain more than one theoretical stage for each combination of mixing and calming sections, and this would be equivalent to reaching equilibrium in the mixing section, and then obtaining an additional amount of extraction by the countercurrent flow through the packing during phase separation. The excess extraction was several times greater than expected from tests using the packing alone in a column. This was doubtless due to the fact that the countercurrent flow in the packing started at the most ideal conditions for efficient extraction, namely, a substantially complete dispersion of the one solvent in the other.

In the 1-in. column, it was possible to obtain a theoretical extraction stage in about 2 in. of height. This is comparable with the heights equivalent to a theoretical plate of the more efficient types of column packing used in this diameter column for distillation. It has been found possible to maintain the same comparison on 12-in. diameter columns (28), so that liquid-extraction columns of fifty or more theoretical

stages may be constructed comparable to distilling columns of fifty or more theoretical plates. Additional data on larger-diameter columns are being obtained to develop the design of the large columns.

The performance of batchwise extraction equipment can be predicted because, as previously mentioned, sufficient time and agitation can be provided to approach equilibrium in each unit. On the other hand, the flow through all countercurrent extraction columns depends upon the properties of the two liquid phases, such as their densities, viscosities, and interfacial tension, as well as the relative flow rates of the phases and diffusivity of the solutes in the solutions. These are intrinsic properties of the system under consideration and different extraction columns perform differently on each system, so that the best type of column for one system of solvents may not be the best for all possible combinations of solutes and solvents. The presence of minute traces of emulsifying agents in either of the solutions greatly affects the performance; in some cases, interchanging the dispersed and continuous phases improves the operation. It is not yet possible to predict the performance of any particular column on a given application without experimental data, and even in these cases, the extrapolation to larger-size columns of the same type is uncertain.

### Applications of Liquid Extraction

The applications of liquid extraction have in the past been limited by the poor performance of the usual equipment to operations involving seven stages or less, and most of the large-scale applications requiring five to seven stages were carried out in individual mixers and settlers.

In spite of these limitations, liquid extraction has been widely used because of the many instances in which separations cannot be carried out by distillation due to the very low volatility of the components, or their instability at the temperatures required for distillation even at the high vacuum available. These difficulties have been discussed under *Distillation*. It will be recognized that, in the previous commercial applications, liquid extraction has only been used as a last resort and has been considered as a rather unsatisfactory unit operation to be avoided wherever possible. The development of a highly efficient type of column such as previously described, will broaden the application of liquid extraction to competition with distillation in separations which are difficult to carry out by the latter operation, and will also make it an invaluable tool for purifying nonvolatile and heat-sensitive compounds, which can only be partially concentrated in present equipment.

One commercial application of liquid extraction is in the recovery of acetic acid from dilute aqueous solutions (see *Acetic acid*). The evaporation of the water from such a solution requires a large amount of heat. In addition, the vapor-liquid equilibrium curve for this system is such that a high reflux ratio is required to remove the water with substantially no acetic acid content; this is essential for a high yield of the acid from the dilute concentration. The extraction of acetic acid from water by a solvent from which it is easier to recover the acetic acid has been the subject of considerable investigations, and practically every available solvent which is immiscible with water has been considered for this purpose. An obviously desirable solvent would be one in which the acetic acid is more soluble than in the water so that the concentration will be increased by extraction, and one which is less volatile than the acetic acid and easily separated by distillation so that the acid may be removed by distillation



at a relatively low reflux ratio. Thus, the evaporation of 2% of the acetic acid at a 5:1 reflux ratio represents a tremendous saving over evaporating 98% of water from the aqueous solution at a 10:1 reflux ratio. Practically any solvent will effect some saving in this process. Liquid extraction with a solvent which may be used subsequently for azeotropic dehydration has also been considered (35-37).

The most important commercial applications of liquid extraction at the present time are in the refining of mineral oil and vegetable oil. In the refining of the lubricating-oil fraction of the crude mineral oil, solvents such as nitrobenzene, furfural, phenol, and sulfur dioxide (Edleanu process) have been used to remove the naphthenic, aromatic, and asphaltic constituents from the desirable paraffinic fraction of the oil by simple extraction (22). Phenol has also been used in liquid extraction with reflux. In this case, the reflux is produced by adding a small amount of water to the phenol extract to precipitate some of the undesirable constituents from the extract solution, and they pass upward through the column to remove the paraffinic constituents from the phenol solution (22). The Duo-Sol process for refining lubricating oils is the only commercial application of fractional liquid extraction with two solvents. The solvents in this case are propane and a cresylic acid mixture, called Selecto, which consists of phenols, cresols, and xlenols. The propane shows a preferential solubility for the paraffinic constituents of the crude, and the Selecto has a preferential solubility for the naphthenic and asphaltic constituents. The process is operated with seven mixing and separating stages and is generally carried out with seven pumps and two large tanks, which are partitioned off to provide the necessary number of settling chambers. The process has not as yet been commercially operated in a single column because it had not previously been possible to obtain this number of equilibrium stages in a packed column of reasonable height. Compare the process of propane deasphalting (see Vol. 2, pp. 177-79).

Another industrial application of liquid extraction has been in the refining of vegetable oils by the use of propane and by the use of furfural. The first of these processes is called the Solexol process, and the reflux is produced by changing the temperature at the end of the column where the propane is discharged, to precipitate some of the vegetable oil as reflux. In most cases, this type of internal reflux would be obtained by cooling since solubility usually decreases with decreasing temperature. However, in this case, the solubility in the propane decreases as the critical temperature of the propane is approached, and the reflux is produced by heating; the separation is carried out in a packed column. Several commercial installations have been made. However, the use of a highly flammable solvent, such as propane, at close to its critical temperature and pressure is one objection that has been raised by potential users of this process. The process is inoperable at conditions appreciably below the critical point of propane because of the complete miscibility of the vegetable oil with the propane. However, the use of two solvents, such as hexane, a higher-boiling paraffin, with a second immiscible solvent could similarly be applied to the refining of vegetable oils and this process would eliminate the hazards of the Solexol process.

Because of its completely general application, fractional liquid extraction can be applied to any separation. It has been demonstrated on mixtures of structural isomers, of different homologs, and of different types of compounds. Its outstanding advantages are in the cases of nonvolatile and heat-sensitive compounds. Previous application of the process has been limited by the inefficient performance of liquid extraction columns, since most such applications require more than ten equilibrium

stages for a good separation. This number of stages, and more, are easily obtained in a single column of a type recently described, and thus, the process of fractional liquid extraction may be considered in many cases where ordinary distillation is difficult.

No applications have as yet been made involving the use of fractional liquid extraction for the separation of azeotropes or close-boiling compounds, and these problems have been solved in large-scale operations by extractive distillation. However, the advantages of liquid extraction in this field have been discussed, and several applications have been proposed which are practical in an efficient type of liquid-extraction column containing a large number of equilibrium stages.

Liquid extraction is widely used in the synthesis and recovery of pharmaceutical compounds, such as the antibiotics penicillin and streptomycin, the alkaloids, the vitamins, and the hormones. The advantage of liquid extraction in this field is that it provides a method of purification and concentration without the use of high temperatures. The temperatures in this case can be regulated by the choice of solvent and by the use of vacuum in evaporating the solvents. The potentialities of a more efficient extraction column in these processes also represent a broad and not yet fully explored field of liquid-liquid extraction applications.

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**EYE LOTIONS.** See *Cosmetics*, Vol. 4, p. 541.



**FACE POWDER.** See *Cosmetics*, Vol. 4, p. 512.

**FACTICE.** See *Drying oils*, Vol. 5, p. 297.

**FARINA.** See *Cereals*, Vol. 3, p. 630.

**FAST COLOR SALTS.** See *Azo dyes*, Vol. 2, p. 255; *Diazo compounds*, Vol. 5, p. 48.

**FAT ACIDS.** See *Fatty acids*.

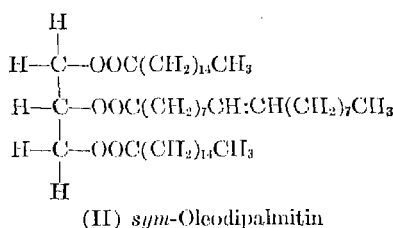
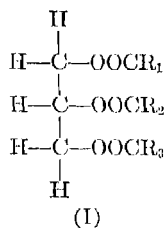
## FATS AND FATTY OILS

Fats and oils constitute a well-defined class of neutral substances, soluble in ether and other organic solvents but not in water, that are produced in some quantity by all plants and animals. Commercial fats and oils are derived, however, from a relatively few members of the plant and animal kingdom, in which they appear in quantity and in an easily available form. They are primarily a product of agriculture, although there is also a considerable production from uncultivated tropical plants and from marine animals.

Except for minor amounts of impurities, some of which are removable by refining treatment, fats and oils consist of triglycerides (see formula (I)), or esters of glycerol (*q.v.*) and high-molecular or long-chain aliphatic acids, both saturated and unsaturated, known as fatty acids (*q.v.*). Waxes (*q.v.*) differ from fats in that they are esters of certain higher monohydric alcohols rather than of glycerol. Wool grease (*q.v.*) or fat, also called degrease, is chiefly a wax, as is also sperm oil. Because the fatty acid radicals constitute the greater part (usually about 95% by weight) of the glyceride molecule, and also the reactive portion, the chemical and physical properties of a fat or oil are determined largely by the properties of the component fatty acids. In general, fats become progressively higher melting and more easily solidified as the average molecular weight of the fatty acids increases and as their average unsaturation (number of double bonds) decreases. There is no rigid distinction to be made between

"oils," which are liquid, and "fats," or "butters" or "tallows," which are solid or semisolid at ordinary atmospheric temperatures; for example, coconut oil is sometimes called coconut butter. For simplicity, the term "fat" is often used, and will be used here, in referring to either the liquid or solid forms. Fatty oils are also sometimes called fixed oils to distinguish them from volatile, ethereal, or essential oils (see *Oils, essential*). (For mineral or hydrocarbon oils, see *Lubrication and lubricants*; *Petroleum*; *Shale oil*.)

Fats are to be classed with proteins and carbohydrates as one of the basic food materials, and are consumed in great quantity in fatty foods and in certain edible prepared fat products (see *Dairy products*; *Margarine*; *Meat and meat products*; *Salad dressings*; *Shortenings*). They are the most concentrated source of energy in the diet, yielding about 9.3 kg.-cal./gram, as compared to 4.1 kg.-cal./gram for proteins or carbohydrates, and are also important as a source of oil-soluble vitamins (see *Fish-liver oils*; *Vitamins*) and of certain essential unsaturated fatty acids.



The similarly large technical or nonedible use of fats is based largely upon: (1) the property of the more unsaturated members of polymerizing to form elastic but durable protective coatings (see *Coatings*; *Drying oils*; *Linoleum*; *Paint*; *Printing inks*; *Varnishes*), and (2) the long-chain character of the fatty acids, which confers surface activity upon many of their derivatives (see *Detergency*; *Emulsions*; *Soap*; *Surface-active materials*). In the manufacture of soap, as well as many other surface-active materials, fats are important not as such, but as a source of fatty acids (see "Manufacture from fats" under *Fatty acids*). Where the fatty acids alone are utilized, glycerol is a valuable by-product.

In certain industrial applications, and for edible use as well, the lubricating or plasticizing properties of fats or fatty acids are important (see *Bakery processes and products*; *Fatty acids*; *Lubrication and lubricants*; *Plasticizers*).

### Composition

**Fatty Acids and Glycerides** (see *Fatty acids*; *Glycerol*). Owing to the complexity of glyceride structure and the present impossibility of accurately determining the composition of a fat in terms of all the component glycerides, chemical analyses of fats usually show only the relative proportions of the different fatty acids. Actually the characteristics and particularly the physical properties of a fat are considerably dependent upon how the fatty acids are distributed within the glyceride molecules (see formula (II) for a typical triglyceride). Hilditch and co-workers (20) have shown that in vegetable fats, and particularly in seed fats, there is a marked tendency for any given fatty acid to be distributed as evenly as possible among the different glycerides, so that simple triglycerides (containing a single fatty acid) do not usually occur in any quantity unless the molar proportion of any one acid exceeds two-thirds of the whole,

TABLE I. Iodine and Saponification Values and Fatty Acid Compositions of Representative Samples of Common Vegetable and Land-Animal Fats and Oils.

Fat or oil	Iodine value	Saponi- fication value	Fatty acid composition, % by wt.										Other acids
			Saturated acids					Monoethenoid acids <sup>a</sup>					
			C <sub>12</sub> (lauric)	C <sub>14</sub> (myristic)	C <sub>16</sub> (palmitic)	C <sub>18</sub> (stearic)	C <sub>18</sub> (arachidic)	C <sub>16</sub> (palmitoleic)	C <sub>18</sub> (oleic)	Dienethenoid acids, C <sub>18</sub> (linoleic)	Triethenoid acids, C <sub>18</sub> (linolenic)		
Almond oil	95	190	—	1.2	4.5	—	—	—	77.0	17.3	—	—	—
Apricot-kernel oil	108.7	190	—	—	2.6	1.2	—	—	64.4	31.8	—	—	—
Babassu oil	16.1	249	44.1	15.4	8.5	2.7	0.2	—	16.1	1.4	—	—	Caproic, 0.2; caprylic, 4.8; capric, 6.6
Borneo tallow	33.2	193	—	—	18.0	43.3	1.1	—	37.4	0.2	—	—	—
Butterfat (cow)	32.9	237	4.5	14.6	30.2	10.5	—	5.7	18.7	2.1	—	—	Butyric, 3.5; caproic, 1.4; caprylic, 1.7; capric, 2.6; satd. above C <sub>18</sub> , 1.6; monoethenoid C <sub>10-14</sub> , 2.0; unsatd. C <sub>20-22</sub> , 0.9
Butterfat (goat)	28.8	240	6.0	12.3	27.9	6.0	—	2.6	21.1	3.6	—	—	Butyric, 3.0; caproic, 2.5; caprylic, 2.8; capric, 10.0; satd. above C <sub>18</sub> , 0.6; mono- ethenoid C <sub>10-14</sub> , 1.4; unsatd. above C <sub>18</sub> , 0.2
Candlenut (lumi- bang) oil	164.3	191	—	—	5.5	6.7	0.3	—	10.5	48.5	28.5	—	—
Castor oil	85.8	195	←	—	2.4	—	→	—	7.4	3.1	—	—	Ricinoleic, 87.0; di- hydroxystearic, 0.6
Chinese vegetable tallow	22.1	204	1.2	2.9	63.1	3.2	—	—	29.6	—	—	—	—
Cocoa butter	36.7	194	—	—	24.4	35.4	—	—	33.1	2.1	—	—	—
Cocunut (copra) oil	8.7	257	48.0	17.5	9.0	2.1	—	—	5.7	2.6	—	—	Caprylic, 7.9; capric, 7.2
Cohune oil	9.8	251	46.4	16.1	9.3	3.3	—	—	9.9	0.9	—	—	Caprylic, 7.5; capric, 6.6
Corn oil	127.1	189	—	0.1	8.1	2.5	—	1.2	30.1	56.3	—	—	Satd. and unsatd. above C <sub>18</sub> , 1.7
Cottonseed oil	105.0	196	—	1.4	23.4	1.1	1.3	2.0	22.9	47.8	—	—	Tetradecenoic, 0.1
Grapefruit-seed oil	100.8	197	—	1.2	27.5	2.9	2.1	—	21.1	39.3	5.9	—	—

Fatty acid composition, % by wt.

Fat or oil	Iodine value	Saponification value	Saturated acids					Monoethenoid acids		Diethenoid acids, C <sub>18</sub> (linoleic)	Triethenoid acids, C <sub>18</sub> (linolenic)	Other acids
			C <sub>12</sub> (lauric)	C <sub>14</sub> (myristic)	C <sub>16</sub> (palmitic)	C <sub>18</sub> (stearic)	C <sub>18</sub> (arachidic)	C <sub>18</sub> (palmitoleic)	C <sub>18</sub> (oleic)			
Hempseed oil	167.0	190	←	←	10	←	→	—	16	46	28	
Kapok oil	96.0	192	—	—	10.4	8.6	—	1.2	46.2	33.6	—	
Lard (European)	59.8	196	—	1.3	28.3	11.9	—	2.7	47.5	6.0	—	Tetradecenoic, 0.2; unsatd. C <sub>20-22</sub> , 2.1
Lard (prime steam, U.S.)	68.5	195	←	←	34.0	←	→	—	52.0	14.0	—	Myristic, 1-2; unsatd. C <sub>20-22</sub> , 1-1.5; arachidonic, 0.2-0.6
Linseed oil	179.8	191	—	—	6.3	2.5	0.5	—	19.0	24.1	47.4	Lignoceric, 0.2
Mowrah (Illipé) fat	63.9	194	—	—	23.7	19.3	—	—	43.3	13.7	—	
Murumuru oil	11.0	242	42.5	36.9	4.6	2.1	—	—	10.8	0.4	—	Caprylic, 1.1; capric, 1.6
Mustardseed oil	103	175	←	←	6	←	→	—	20	16	8	Erucic, 50 (approx.)
Neatsfoot oil	73.3	196	—	0.7	16.9	2.7	0.1	9.4	64.4	2.3	0.7	Tetradecenoic, 1.2; unsatd. C <sub>20-22</sub> , 1.6
Oiticica oil	<sup>a</sup>	192	←	←	11.3	←	→	—	6.2	—	—	Licanic, 82.5
Olive oil	84.2	194	—	1.2	15.6	2.0	—	1.6	64.6	15.0	—	
Orangeseed oil	97.6	196	—	—	23.8	8.3	0.7	—	24.8	37.1	5.3	
Ouricuri oil	14.7	257	45.8	9.0	7.7	2.3	0.1	—	13.1	2.2	—	Caproic, 1.8; caprylic, 9.8; capric, 8.2
Palm oil	52.9	200	—	2.4	41.6	6.3	—	1.8	38.0	9.5	0.4	
Palm-kernel oil	16.3	244	46.9	14.1	8.8	1.3	—	—	18.5	0.7	—	Caprylic, 2.7; capric, 7.0
Peanut oil	93.3	190	—	0.5	7.8	3.1	2.4	1.7	54.3	26.0	—	Behenic, 3.1; lignoceric, 1.1
Perilla oil	207.3	191	←	←	6.6	←	→	—	13.5	14.7	65.2	
Poppyseed oil	133.4	197	←	←	7.2	←	→	—	28.3	58.5	—	
Rapeseed (colza) oil	102.3	175	—	—	1.9	3.5	0.7	1.5	12.3	15.8	8.7	Behenic, 0.7; lignoceric, 0.8; eicosenoic, 4.8; erucic, 47.8; docosadienoic, 1.5

Continued

TABLE I. Iodine and Saponification Values and Fatty Acid Compositions of Representative Samples of Common Vegetable and Land-Animal Fats and Oils (Concluded).

Fat or oil	Iodine value	Saponification value	Fatty acid composition, % by wt.									
			Saturated acids					Monoethenoic acids			Diethenoic acids, C <sub>18</sub> , C <sub>19</sub> (linoleic)	
			C <sub>12</sub> (lauric)	C <sub>14</sub> (myristic)	C <sub>16</sub> (palmitic)	C <sub>18</sub> (stearic)	C <sub>18</sub> (arachidic)	C <sub>18</sub> (palmitoic)	C <sub>19</sub> (oleic)	C <sub>20</sub> (linoleic)	Triethenoic acids, C <sub>20</sub> (linolenic)	Other acids
Ravison oil	108.5	178	—	—	4.3	2.1	1.8	0.6	15.5	20.9	9.9	Behenic, 0.5; lignoceric, 0.6; eicosenoic, 4.1; erucic, 38.7; docosadienoic, 1.0
Rice-bran oil	99.9	185	—	0.5	11.7	1.7	0.5	—	39.2	35.1	—	Lignoceric, 0.4
Safflower oil	136.2	191	0.4	1.1	2.9	1.1	0.5	—	32.8	61.1	0.1(?)	—
Sesame oil	110.6	190	—	0.1	8.2	3.6	1.1	0.5	45.3	41.2	—	—
Shea fat	59.1	184	—	—	5.7	41.0	—	—	49.0	4.3	—	—
Sorghum oil	119.0	191	—	0.2	8.3	5.8	—	0.1	26.2	49.4	—	—
Soybean oil	132.6	193	—	0.4	10.6	2.4	—	1.0	23.5	51.2	8.5	Satd. C <sub>20-23</sub> , 2.4
Sillington oil	185.8	207 <sup>a</sup>	←	—	9	—	→	—	10	30	45	Conjugated decadienoic, 5
Sunflowerseed oil	130.8	188	—	—	3.6	2.9	0.3	—	34.0	57.5	—	Lignoceric, 0.4
Tallow (beef)	44.7	196	0.2	3.1	24.9	24.1	0.8	2.4	41.8	1.8	0.5	Tetradecenoic, 0.4; unsatd. C <sub>20-23</sub> , 0.5
Tallow (goat)	33.5	199	3.5	2.1	25.5	28.1	2.4	—	38.4	—	—	—
Tallow (mutton)	41.2	197	—	4.6	24.6	30.5	—	—	36.0	4.3	—	—
Teaseed oil	86.3	192	—	0.3	7.6	0.8	0.6	—	83.3	7.4	—	—
Tucum oil	15.8	241	48.9	21.6	6.4	1.7	—	—	13.2	2.5	—	Caprylic, 1.3; capric, 4.4
Tung (China wood) oil	—	192	←	—	5	—	→	—	5	3	—	Eleostearic, 87
Ucububa butter	9.9	228	14.8	72.5	4.9	—	—	—	6.3	—	—	Capric, 0.5
Walnut (English) oil	155.7	190	←	—	8.1	—	→	—	19.1	65.9	6.9	—
Wheat-germ oil	128.6	184	←	—	15.5	—	→	—	25.5	52.6	6.3	—

<sup>a</sup> Owing to incomplete halogen absorption, iodine values for conjugated acid oils by the usual methods (Wijs, Hanus, etc.) are both low and variable. The true iodine value of fresh tung oil, as determined by special methods (26), is 248-252; that of olivica oil is 205-220.

whereas any acid comprising more than one-third of the total will tend to appear in all the glycerides. Since trisaturated glycerides have much higher melting points than glycerides containing one or more unsaturated fatty acid radicals, one result of even distribution is to make vegetable fats generally lower melting than animal fats of equivalent fatty acid composition.

**Phosphatides** (see *Lecithin*; *Lipides*). Phosphatides are fat-soluble and, being associated with fats in many plant and some animal tissues, are often found in crude fats (for example, to the extent of 2–3% in soybean and corn oils). They are removed from the oil by “degumming” (hydration) or by acid or alkali refining.

**Antioxidants** (*q.v.*). Most vegetable fats contain minor proportions (0.05–0.20%) of antioxidants, which serve to powerfully inhibit atmospheric oxidation, the cause of rancidity in fats. In animal fats, antioxidants are generally almost entirely absent. The common antioxidants of vegetable fats are tocopherols (see “Vitamin E” under *Vitamins*); in a few cases, antioxidants peculiar to specific fats are known. Antioxidants are not removed to any large extent by refining or other common (edible-oil) processing treatment.

**Pigments.** The characteristic yellow-red color of most vegetable fats and some animal fats is principally derived from carotenoid pigments. Palm oil, which is unusually high in color, contains about 0.20%  $\beta$ -carotene. Olive oil and some seed oils (for example, soybean oil) may contain sufficient chlorophyll or related compounds to produce a greenish tinge. Cottonseed oil (see *Cottonseed*) is strongly colored by pigments of the gossypol type. All of these pigments are readily reduced to low levels by alkali refining of the oil and adsorption bleaching. However, brownish or reddish pigments found in oils derived from damaged materials, which are probably in part protein and carbohydrate decomposition products, are relatively resistant to refining treatment.

The content of carotenoid pigments is lowered by oxidation or by heat treatment, but vegetable oils containing  $\gamma$ -tocopherol darken with limited oxidation, from the formation of chroman-5,6-quinones (derivatives of 5,6-chromandione).

**Vitamins** (*q.v.*). Vitamin A occurs as such in butterfat (see *Dairy products*) and fish-body oils, and in high concentrations in certain fish-liver oils (*q.v.*). The precursor of vitamin A (carotene) occurs in butterfat, in unbleached palm oil, and in traces in other fats. Vitamin D is found in fish-liver oils, fish-body oils, and to some extent in butterfat. As a source of vitamins, the common vegetable oils are important only with respect to their content of tocopherols, which are identical with vitamin E.

**Sterols** (*q.v.*). Most of the 0.5–1.5% unsaponifiable material commonly found in both vegetable and animal fats consists of sterols. The sterols of animal fats, consisting principally of cholesterol, are sufficiently different from the mixture of sitosterols, stigmasterols, etc., in vegetable oils to permit the two classes of fats to be distinguished through the difference in melting points of their sterol acetates (22).

The sterols are colorless and odorless and generally inert in so far as the practical applications of fats are concerned. A portion of the sterols in crude oils is removed by alkali refining; the soap stock or residue from refining serves as a commercial source of sterols for the manufacture of pharmaceuticals.

**Free Fatty Acids.** The free fatty acids content of a crude fat is usually dependent upon the degree to which the fat has been subjected to enzymic hydrolysis in the parent oil-bearing material before extraction. In fats of good quality, it is not ordinarily greater than about 1%, although in fats obtained from damaged materials it



may be much higher. Palm oil and inedible tallow and greases are characteristically high in free fatty acids (3–30%).

**Other minor constituents** of fats and oils consist of traces of hydrocarbons, ketones, and other unidentified materials, which give the individual members their distinctive odors and flavors.

#### COMPOSITION AND CHARACTERISTICS OF INDIVIDUAL FATS AND OILS

The iodine and saponification values and fatty acid compositions reported for representative samples of vegetable and land-animal fats and oils are listed in Table I. In the case of some oils, detailed analyses, including estimates of minor fatty acids, are not available, and contents of minor acids are included with those of related acids, for example, palmitoleic (hexadecenoic) with oleic, and arachidic with stearic. In a few cases, the proportions of acids originally reported have been adjusted to make them conform with later and more accurate but incomplete data. Most of the iodine and saponification values listed are observed values, but a few are calculated.

Corresponding data for marine oils are given in Table II. In these the wide variety of unsaturated fatty acids makes it impossible to determine the proportions of individual acids, and hence only the average degree of unsaturation of the acids of each chain length has been recorded. The average unsaturation is given in each case in terms of deficiency of hydrogen atoms. For monoethenoid acids, for example, it is 2.0, for diethenoid acids, 4.0, etc.

TABLE II. Iodine and Saponification Values and Fatty Acid Compositions of Representative Samples of Marine Oils.

Analysis	Cod-liver	Herring	Monhaden	Sardine, California (pilchard)	Sardine, Japanese	Seal, gray	Whale
Iodine value. . .	155–175	120–145	150–185	170–190	160–190	102.2	110–125
Saponification value. . . . .	185–195	185–195	185–195	185–195	185–195	191	190–200
Saturated acids, % by wt.:							
C <sub>12</sub> . . . . .	—	0.1	—	—	—	—	—
C <sub>14</sub> . . . . .	5.8	7.0	5.9	5.1	5.8	4.7	9.2
C <sub>16</sub> . . . . .	8.4	11.7	16.3	14.6	9.7	12.1	15.6
C <sub>18</sub> . . . . .	0.6	0.8	0.6	3.2	2.3	2.0	1.9
C <sub>20–22</sub> . . . . .	—	0.1	1.4	—	—	0.1	0.6
Unsaturated acids, % by wt.:							
C <sub>14</sub> . . . . .	0.2	1.2 (2.0)	—	—	—	3.3 (2.0)	2.5 (2.0)
C <sub>16</sub> . . . . .	20.0 (2.3)	11.8 (2.4)	15.5 (3)	11.8 (2.0)	13.0 (2)	19.2 (2.2)	13.9 (2.1)
C <sub>18</sub> . . . . .	29.1 (2.8)	19.6 (3.5)	29.6 (4)	17.8 (3.3)	24.2 (3)	31.8 (2.7)	37.2 (2.4)
C <sub>20</sub> . . . . .	25.4 (6.0)	25.9 (5.2)	19.0 (10)	18.1 (4.1)	26.0 (5)	12.9 (5.7)	12.0 (7.1)
C <sub>22</sub> . . . . .	9.6 (6.9)	21.6 (4.3)	11.7 (10)	14.0 (8.5)	19.0 (5)	13.4 (10.6)	7.1 (9.4)
C <sub>24</sub> . . . . .	—	0.1 (3.8)	—	15.4 (10.9)	—	0.5 (11.0)	—

<sup>a</sup> Values in parentheses represent unsaturation of fraction in terms of deficiency of hydrogen (see above).

#### Classification

On the basis of their unsaturation and consequent drying or polymerizing properties, fats and oils are commonly classified as *nondrying* (iodine value below about 90), *semidrying* (iodine value about 90–130), and *drying* (iodine value above about 130) (see *Drying oils*). A more rational classification (3), based upon chemical composition

TABLE III. Classification, Sources, and Production of Commercially Important Vegetable Oils.

Fat or oil	Type or group	Botanical name of plant <sup>a</sup>	Principal geographical sources	Normal world production <sup>b</sup>
Almond oil <sup>c</sup>	Oleic-linoleic acid	<i>Prunus amygdalus</i>	Europe, Africa, U.S.	Very small
Apricot-kernel oil <sup>c</sup>	Oleic-linoleic acid	<i>Prunus armeniaca</i>	U.S., Europe	Very small
Babassu oil	Lauric acid	<i>Orbignya (Attalea) speciosa</i>	Brazil	Small
Borneo tallow	Vegetable butter	<i>Shorea stenoptera</i>	East Indies, Malaya	Probably very small
Candlenut (lumbang) oil	Linolenic acid	<i>Aleurites maluccana</i>	Philippines, South Pacific region	Probably very small
Castor oil	Hydroxy acid	<i>Ricinus communis</i>	Brazil, India, U.S.S.R., Manchuria	Large
Chinese vegetable tallow	Vegetable butter	<i>Stillingia sebifera</i>	China	Probably very small
Cocoa butter <sup>c</sup>	Vegetable butter	<i>Theobroma cacao</i>	Africa, Brazil, Central America	Small
Coconut (copra) oil	Lauric acid	<i>Cocos nucifera</i>	Philippines, East Indies, other South Pacific islands, Ceylon	Very large
Cohune oil	Lauric acid	<i>Attalea cohune</i>	Central America	Very small
Corn oil <sup>c</sup>	Oleic-linoleic acid	<i>Zea mays</i>	U.S., Europe, Argentina	Large
Cottonseed oil <sup>c</sup>	Oleic-linoleic acid	<i>Gossypium hirsutum</i> , <i>G. barbadense</i>	U.S., India, Brazil, U.S.S.R., China, Egypt, etc.	Very large
Grapefruit-seed oil <sup>c</sup>	Linolenic acid	<i>Citrus paradisi</i>	U.S.	Very small
Hempseed oil <sup>c</sup>	Linolenic acid	<i>Cannabis sativa</i>	Europe, Asia	Probably small
Kapok oil <sup>c</sup>	Oleic-linoleic acid	<i>Eriodendron anfractuosum</i>	Indonesia	Probably very small
Linseed oil	Linolenic acid	<i>Linum usitatissimum</i>	Argentina, U.S., Canada, U.S.S.R., India	Very large
Mowrah (illipe) fat	Vegetable butter	<i>Bassia longifolia</i> , <i>B. latifolia</i>	India	Probably very small
Murumuru oil	Lauric acid	<i>Astrocaryum murumuru</i>	Brazil	Very small
Mustardseed oil	Erucic acid	<i>Brassica nigra</i>	Europe, India	Probably small
Oiticica oil	Conjugated acid	<i>Licania rigida</i>	Brazil	Very small
Olive oil	Oleic-linoleic acid	<i>Olea europæa</i>	Spain, Italy, North Africa, Greece	Very large
Orangeseed oil <sup>c</sup>	Linolenic acid	<i>Citrus sinensis</i>	U.S.	Very small
Ouricuri oil	Lauric acid	<i>Syagrus coronata</i>	Brazil	Very small
Palm oil	Oleic-linoleic acid	<i>Elæis guineensis</i>	Africa, Indonesia, Malaya	Very large
Palm-kernel oil	Lauric acid	<i>Elæis guineensis</i>	Africa, Indonesia, Malaya	Large
Peanut oil	Oleic-linoleic acid	<i>Arachis hypogæa</i>	Africa, India, China, U.S., etc.	Very large
Perilla oil	Linolenic acid	<i>Perilla ocymoides</i>	Manchuria, Korea, Japan, India	Small
Poppyseed oil	Oleic-linoleic acid	Varieties of Papaveraceæ	Europe, U.S.S.R., Asia	Probably small
Rapeseed (colza) oil	Erucic acid	<i>Brassica campestris</i>	Europe, India, China, Japan	Probably large
Ravison oil	Erucic acid	Varieties of <i>Brassica campestris</i>	Black Sea region	Probably small
Rice-bran oil <sup>c</sup>	Oleic-linoleic acid	<i>Oryza sativa</i>	Japan, U.S., China	Probably very small
Safflower oil	Oleic-linoleic acid	<i>Carthamus tinctorius</i>	India, Egypt, U.S.S.R.	Probably small
Sesame oil	Oleic-linoleic acid	<i>Sesamum indicum</i>	China, India, Africa, Mexico, etc.	Large
Shea fat	Vegetable butter	<i>Butyrospermum parkii</i>	Africa	Probably very small
Soybean oil	Linolenic acid	<i>Soja max</i>	U.S., China, Manchuria	Very large
Stillingia oil	Conjugated acid	<i>Stillingia sebifera</i>	China	Probably very small
Sunflowerseed oil	Oleic-linoleic acid	<i>Helianthus annuus</i>	Argentina, U.S.S.R., Baltic region, Canada	Probably large
Teaseed oil	Oleic-linoleic acid	<i>Thea sasanqua</i>	China	Very small to small
Tucum oil	Lauric acid	<i>Astrocaryum tucuma</i>	Brazil	Very small
Tung (China wood) oil	Conjugated acid	<i>Aleurites fordii</i> , <i>A. montana</i>	China, small production in U.S. and South America	Small to large
Ucuhuba butter	Vegetable butter	<i>Virola sebifera</i> , <i>V. surinamensis</i>	Brazil	Very small
Walnut (English) oil <sup>c</sup>	Linolenic acid	<i>Juglans regia</i>	Central Europe, Asia, U.S.	Probably very small
Wheat-germ oil <sup>c</sup>	Linolenic acid	Varieties of <i>Triticum</i>	U.S., Canada, etc.	Very small

<sup>a</sup> All of the oils listed are derived from the seed kernels of the plants, with the exception of Chinese vegetable tallow, olive oil, and palm oil, which are fruit-coat oils.

<sup>b</sup> Production of the different oils is rated approximately as follows (per annum basis): over 1 billion pounds, very large; 200 million to 1 billion pounds, large; 50 to 200 million pounds, small; under 50 million pounds, very small.

<sup>c</sup> Plant cultivated or processed primarily for products other than oil.

and industrial applications, places the commercially important fats and oils in the following groups (see Table III).

**Milk fats** are distinguished by low unsaturation and the presence of a wide variety of saturated fatty acids of short chain length. *Butterfat* (of the cow) is the only important member; it is relatively expensive and is used only for edible purposes.

**Lauric acid oils** are distinguished by very low unsaturation and a high content of lauric acid, as well as other short-chain acids. They melt sharply at relatively low temperatures and are relatively light colored and low in nonglyceride constituents. Lauric acid oils are derived from seeds of cultivated or noncultivated palms. The important members are *coconut* and *palm-kernel* oils; they are normally cheap and are used for soapmaking and also for edible products.

**Vegetable butters** are low in unsaturation and contain principally  $C_{14}$ - $C_{18}$  acids. The relatively low melting points and very sharp melting of these butters are due to the even distribution of saturated and unsaturated fatty acids, rather than to the presence of low-molecular acids, as in lauric acid oils. Vegetable butters are derived from seeds of tropical trees. *Cocoa butter* is the most important member; it is expensive and is used principally in confectionery (see *Chocolate and cocoa*).

**Land-animal fats** are relatively low in unsaturation and contain principally  $C_{16}$  and  $C_{18}$  acids. The unsaturated acids consist almost entirely of oleic and linoleic acids. With saturated and unsaturated acids unevenly distributed, they exhibit gradual melting and relatively high melting points. If derived from undamaged materials, they are light colored and low in nonglyceride constituents; inedible grades are often dark colored. *Lard* (from hogs) and *tallow* (from cattle and sheep) are derived principally from body fat as a by-product of meat packing (see *Meat and meat products*). They are relatively cheap and are used as edible fats, as a source of commercial fatty acids (see "Manufacture from fats" under *Fatty acids*), and for soapmaking. The term "grease" refers to the softer inedible fats used principally by soapmakers; a fat with a titer below  $40^{\circ}\text{C}$ . is considered a grease, and a fat with a titer over  $40^{\circ}\text{C}$ . is classed as an inedible tallow.

**Oleic-linoleic acid oils** are of medium but rather variable unsaturation (iodine value varies from about 50 for palm oil to about 120 for corn and sunflowerseed oil), with no fatty acids more unsaturated than linoleic (two double bonds); the fatty acids are predominantly  $C_{18}$ . These oils are normally liquid in the raw form, but are frequently hydrogenated to produce plastic fats. The crude seed oils are relatively high in nonglyceride substances. They are derived principally from fruit pulp of perennial plants (*palm, olive*), and seed of cultivated annual plants (for example, *cottonseed, peanut, sunflowerseed, corn, sesame*). The oils are of medium price and are used principally for edible purposes (palm oil is considerably used in soapmaking).

**Erucic acid oils** resemble in composition the oleic-linoleic acid oils, except that the predominant unsaturated fatty acid is a  $C_{22}$  monoethenoid acid, erucic, and there is a minor proportion (6-10%) of linolenic acid. The commercially important members, *rapeseed (colza)*, *ravison*, and *mustardseed*, are used in Europe and Asia as edible oils, but in the U.S. they are used only for technical purposes, that is, for sulfonation (see *Surface-active materials*), and in the manufacture of lubricants (see *Lubrication and lubricants*), and factice (see *Drying oils*, Vol. 5, p. 297). They are derived from the seeds of cultivated annual plants.

**Linolenic acid oils**, derived almost wholly from the seeds of cultivated annual plants, are generally similar to the oleic-linoleic acid oils, but are distinguished from

the latter by containing a more highly unsaturated acid, linolenic (three double bonds). The most important members are *soybean* and *linseed*, which are medium-priced oils. Soybean oil is used both in edible products and as a drying oil, but linseed, except in the Baltic region, is considered strictly a drying oil (see *Drying oils*). Linolenic acid oils or other oils containing a substantial proportion of unsaturated acids with more than two double bonds are less desirable than other fats for the manufacture of edible products because of their flavor instability or tendency toward "flavor reversion" after deodorization.

**Conjugated acid oils** are used only as drying oils (*q.v.*), for which they are particularly suited because of their high content of unsaturated fatty acids with conjugated double bonds. The commercially important members, *tung* and *oilicica*, are derived from the seeds of subtropical trees. They are relatively high priced.

**Marine oils** (see "Marine-oil fatty acids" under *Fatty acids*; *Fish*) are distinguished by their considerable content of fatty acids that vary considerably in chain length, ranging both above and below  $C_{18}$ , and by the presence of highly unsaturated acids (four or more double bonds) together with a considerable content of saturated acids (as much as 25% of the total acids). Although used for edible purposes, as drying oils, and, after hydrogenation, for soapmaking including the manufacture of metallic soaps (see *Driers and metallic soaps*), the diversity of their component fatty acids prevents them from being the most highly desirable materials for any particular purpose, and they are generally the cheapest of all fats and oils. Large quantities of these are used in the fat liquoring of leather.

Unlike the land-animal fats, marine oils are not a by-product of food processing. The commercially important members are derived from the *whale*, and from small oily fishes such as *California sardine* (*pilchard*), *menhaden*, and *herring*, which are taken primarily for their oil. (Sperm whale oils are actually in large part liquid waxes. The body and head oils are composed of approximately 65 and 74% of esters of normal higher monohydric alcohols, and 35 and 26% of esters of glycerol, respectively.) Fish-liver oils (*q.v.*), derived from entirely different species of fish (since oily fish generally have livers with a low oil content and vice versa), are important as the only commercial source of natural vitamin A.

**Hydroxy acid oils** are represented by *castor* oil (*q.v.*), which consists principally of glycerides of ricinoleic (12-hydroxyoleic) acid. Castor oil is used (after "dehydration") as a drying oil of the conjugated type, and for the manufacture of a number of specialty products.

## Properties

### PHYSICAL AND THERMAL PROPERTIES

**Viscosity.** On a loglog scale, the viscosity-temperature relationship of a fatty oil approaches a straight line, with a slope less than that of mineral oils. The curves for hydrogenated cottonseed oil at three different iodine values (32,38) and for oleic acid in Figure 1 are representative of oils containing principally  $C_{16}$  and  $C_{18}$  acids. As the viscosity is somewhat dependent upon the average molecular weight as well as the unsaturation, coconut oil, for example, is about one-third less viscous than hydrogenated cottonseed oil of the same iodine value, and rapeseed oil is about one-third more viscous. Because of its content of hydroxy acids, castor oil is much more viscous than ordinary oils (600–800 centipoises at 25°C. and 15–20 centipoises at 100°C.).

The viscosity of an oil is increased markedly by polymerization. In the range 25–100°C., the viscosity of an oil is roughly twice that of the corresponding free fatty acids.

**Surface and Interfacial Tensions.** The surface tension of a refined oil such as cottonseed oil is about 35 dynes/cm. and the interfacial tension against water is about 30 dynes/cm. at 60–70°C. Both decrease slowly with increase in the temperature; for example, the surface tension at 200°C. is about 30 dynes/cm.

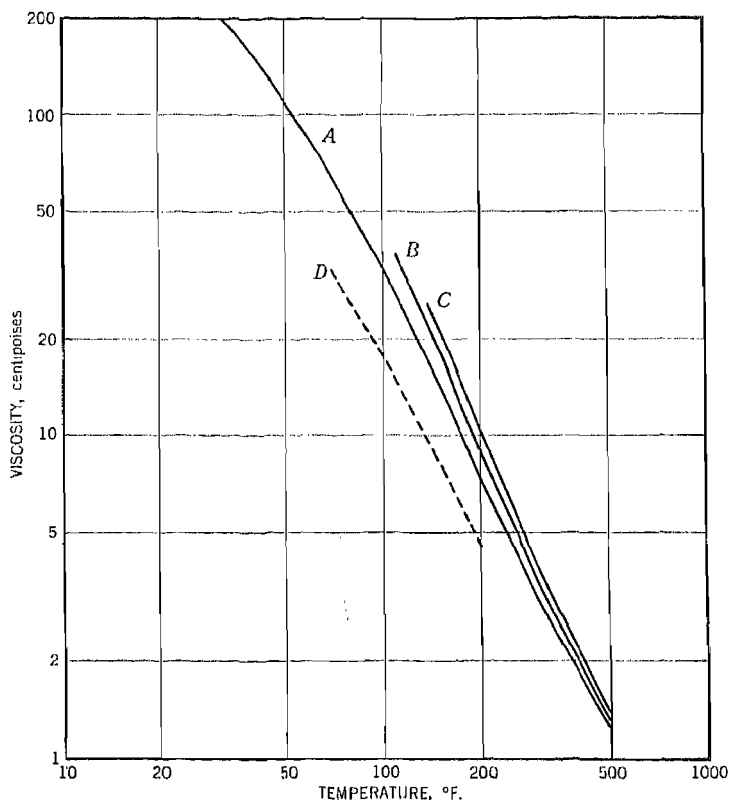


Fig. 1. Viscosity-temperature curves for: *A*, cottonseed oil (iodine value = 110); *B*, partially hydrogenated cottonseed oil (iodine value = 66); *C*, highly hydrogenated cottonseed oil (iodine value = 6); and *D*, oleic acid.

**Crystal Formation.** Most natural fats contain a great diversity of high- and low-melting glycerides, which melt or solidify over a wide range of temperatures. Limited cooling of a liquid fat results in the deposition of the higher-melting glycerides in the form of needlelike crystals, which interlace and cohere to form a plastic material with the lower-melting liquid glycerides. The plasticity of fats, which thus changes progressively with temperature, is a highly important property of many industrial fat products (see *Margarine*; *Shortenings*). To a large degree, the size of the crystals and the plasticity are dependent upon the rate of cooling, with the smallest crystals being produced by rapid cooling. Marked supercooling is characteristic of fats.

Pure triglycerides are polymorphic, that is, they are capable of existing in more than

one crystal form, each of which has a distinctive melting point, density, heat of fusion, etc. (7). Tristearin, for example, crystallizes in three forms,  $\alpha$ ,  $\beta'$ , and  $\beta$ , with melting points of 54, 64, and 73°C., respectively. The lower-melting metastable forms, which tend to crystallize from rapidly cooled melts, transform irreversibly to the stable highest-melting form when heated slowly; however, rapid heating may cause melting before transformation can occur. Polymorphism is not ordinarily observed in the complex glyceride mixtures comprising most commercial fats, but it may be prominent in fats that consist predominantly of one glyceride or class of glycerides (for example, cocoa butter, oleo oil (expressed from oleostock, a high grade of edible tallow), and highly hydrogenated vegetable oil), where it may produce "double melting" and other anomalous effects.

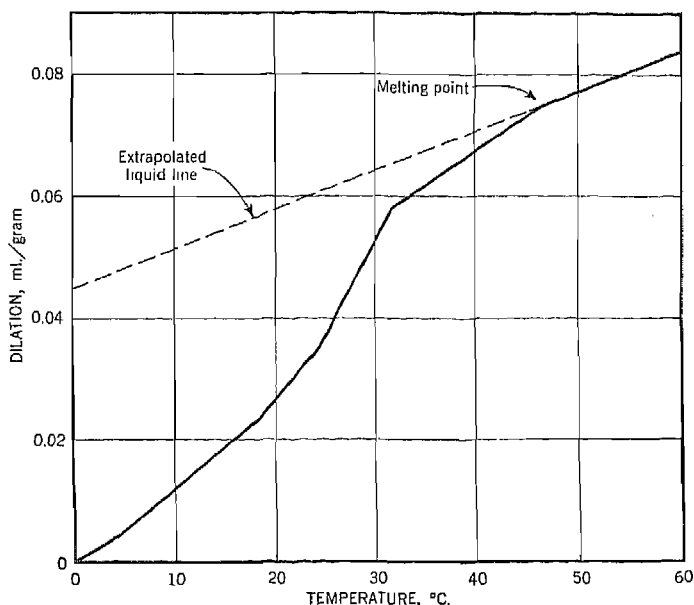


Fig. 2. Dilatometric curve of prime steam lard. (Distance of dilatometric curve from extrapolated liquid line is a measure of the amount of solid or crystalline material.)

**Melting and Solidification Points.** In general, triglycerides reflect the melting points of their constituent fatty acids (*q.v.*). Therefore, a low degree of unsaturation, a high molecular weight, and the presence of trans rather than cis isomers of unsaturated acids, all contribute to a relatively high melting point. The melting points (of the stable form) of representative pure triglycerides are given in Table IV. The final melting point of a commercial fat that melts over a range of temperatures is difficult to determine by the ordinary capillary tube method; in addition, it is not always a highly important characteristic, as the practical fat processor or user is often more concerned with the consistency of the fat at some temperature short of that representing complete liquefaction. Most of the melting point methods for commercial fats, including the widely used *Wiley melting point method* (1) (see "Fats and oils" under *Food analysis*), actually determine the temperature at which there is an arbitrarily

established degree of softening or near-melting. The melting behavior of a typical plastic fat, as revealed by dilatometric measurements, is shown in Figure 2 (26).

TABLE IV. Melting Points of Pure Triglycerides.

Triglyceride	M.p., °C.	Triglyceride	M.p., °C.
Tristearin.....	73.1	<i>sym</i> -Palmitodistearin.....	68.5
Tripalmitin.....	66.4	<i>unsym</i> -Palmitodistearin.....	65.2
Trimyristin.....	57.0	<i>unsym</i> -Stearodipalmitin.....	62.7
Trilaurin.....	46.5	Palmitomyristolaurin.....	49.0
Triolein.....	5.5	<i>sym</i> -Oleodistearin.....	43.5
Trielaidin.....	42.0	<i>sym</i> -Oleodipalmitin.....	37.5
Trilinolein.....	-13.1	<i>unsym</i> -Stearodiolein.....	23.5
Trilinolenin.....	-24.2	<i>unsym</i> -Palmitodiolein.....	19.0

The final melting point at which all crystals disappear from the fat is a useful characteristic of hard butters, highly hydrogenated fats, and other fats in which melting occurs with reasonable abruptness, rather than gradually. The final melting points of average samples of certain of these and other fats are given in Table V.

TABLE V. Final Melting Points of Average Samples of Fats.

Fat or oil	M.p., °C.	Fat or oil	M.p., °C.
Babassu oil.....	26	Palm oil (refined).....	40
Beef tallow.....	50	Palm-kernel oil.....	29
Borneo tallow.....	38	Peanut oil.....	13
Butterfat.....	37	<i>Hydrogenated oils</i>	
Cocoa butter.....	36	Castor oil.....	87 <sup>a</sup>
Coconut oil.....	26	Cottonseed oil.....	60.0 <sup>b</sup>
Cottonseed oil.....	11	Sardine oil.....	57.5 <sup>b</sup>
Lard, prime steam, U.S.....	45	Soybean oil.....	66.5 <sup>b</sup>

<sup>a</sup> Iodine value = 0.5.

<sup>b</sup> Iodine value = 10.

The solidification point of a commercial fat or other mixture is characteristic only if the determination is carried out under carefully standardized conditions. The solidification point is not often determined on fats as such except for the control of commercial hydrogenation (the so-called *congeal point*), but it is a useful characteristic of the separated fatty acids when the fat is to be used for soapmaking or fatty acid manufacture. The solidification point of the mixed fatty acids, or the maximum temperature to which the acids are carried by heat of crystallization when a sample of given size is solidified under specified conditions, is known as the *titer* of the fat. The usual ranges of titers for different fats are given in Table VI.

**Density.** There are no great differences in the densities of different fats and oils in the liquid state, although both the degree of unsaturation (as measured by the iodine value) and the average molecular weight (as measured by the saponification value) affect this property slightly. The following relationship may be derived from the correlation given by Lund (31):  $d^{15} = 0.8467 + 0.00030(\text{saponification value}) + 0.00014(\text{iodine value})$ . Because of the unusual structure of their fatty acids, conjugated acid oils and hydroxy acid oils do not conform to this relationship. The density of most oils, over the range of temperatures to which oils are ordinarily heated

in processing (about 50–500°F.), varies linearly with temperature at the rate of about 0.00064/°C. or 0.000355/°F. Representative values for the density at 60°C. are given in Table VII.

TABLE VI. Ranges of Titters for Different Fats.

Fat or oil	Titer range, °C.	Fat or oil	Titer range, °C.
Babassu oil.....	21–24	Palm-kernel oil.....	22–26
Beef tallow.....	40–46	Peanut oil.....	28–32
Castor oil.....	2–4	Rapeseed oil.....	12–14
Coconut oil.....	21–24	Sardine oil.....	28–32
Corn oil.....	16–20	Sesame oil.....	20–24
Cottonseed oil.....	32–36	Soybean oil.....	22–26
Greases, inedible.....	36–40	Sunflowerseed oil.....	16–20
Lard.....	36–42	Whale oil.....	22–24
Linseed oil.....	18–21	<i>Hydrogenated oils</i>	
Menhaden oil.....	30–34	Sardine oil.....	53.5 <sup>a</sup>
Olive oil.....	18–24	Soybean oil.....	64.5 <sup>a</sup>
Palm oil.....	42–46	Tallow.....	58.5 <sup>a</sup>

<sup>a</sup> Iodine value = 6.

TABLE VII. Densities of Representative Samples of Fats at 60°C.

Fat or oil	d <sub>60</sub>	Fat or oil	d <sub>60</sub>
Castor oil.....	0.932	Lard.....	0.889
Coconut oil.....	0.895	Linseed oil.....	0.903
Cottonseed oil.....	0.895	Rapeseed oil.....	0.886
Cottonseed oil, hydrogenated <sup>a</sup> .....	0.880	Tung oil.....	0.912

<sup>a</sup> Iodine value = 6.

Fats contract considerably upon solidification (about 5–15%), with the contraction being greatest for those most highly saturated (8); hence the density of a partially solidified (plastic) fat depends largely upon the relative proportions of solids and liquid. At –40°C., the density of completely solidified lard or similar hydrogenated vegetable oil is about 1.000, and that of a highly hydrogenated oil such as cottonseed oil is about 1.022. The change of density of the solid material is of the order of 0.00030–0.00035/°C.

**Specific Heat and Heat of Fusion.** The specific heat of liquid fats increases slightly with decrease in the iodine value and varies almost linearly with the temperature. Values reported for different fats are approximately as given in Table VIII (14).

TABLE VIII. Specific Heats of Representative Samples of Oils.

Oil	Specific heat at:	
	40°C.	200°C.
Castor oil.....	0.52	0.59
Cottonseed oil, hydrogenated <sup>a</sup> .....	0.50	0.60
Soybean oil and linseed oil.....	0.48	0.58
Tung oil.....	0.46	0.55

<sup>a</sup> Iodine value = 6.5.



The heat of fusion is a function of the compactness of the fat crystals, being higher for fats of high molecular weight than those of low molecular weight, higher for simple than for mixed saturated triglycerides, and higher for saturated than for unsaturated glycerides. Heats of fusion of pure trilaurin, trimyristin, tripalmitin, and tristearin are 46.2, 50.3, 53.1, and 54.5 gram-cal./gram, respectively (13). Reported values for raw cottonseed oil, partially hydrogenated cottonseed oil (iodine value = 59.5), and highly hydrogenated cottonseed oil (iodine value = 0.9) are 20.6, 27.4, and 44.3 gram-cal./gram, respectively (35). For data for calculations involving melting of these materials, the original articles should be consulted, as plastic fats are not completely solidified except at very low temperatures, and the calculated heat of fusion varies according to the temperature at which melting is assumed to occur.

**Vapor Pressure.** The vapor pressures of triglycerides are very low. Reported values, in mm. Hg, include the following (36): tristearin, 0.001 at 253°C. and 0.050 at 313°C.; trilaurin, 0.001 at 188°C. and 0.050 at 244°C.; soybean oil and olive oil, 0.001 at 253°C. and 0.050 at 308°C.

**Heat of Combustion.** Bertram (10) has given the following formula for calculating the approximate heat of combustion of fatty oils, in gram-cal./gram, in terms of constant volume at 15°C.: heat of combustion = 11,380 - (iodine value) - 9.15 × (saponification value). A value of 9500 gram-cal./gram is ordinarily taken for common edible fats such as lard and cottonseed oil.

**Smoke, Fire, and Flash Points.** The smoke, fire, and flash points of a fat are determined primarily by its content of free fatty acids. Average values for common fats containing principally C<sub>16</sub> and C<sub>18</sub> acids are approximately as given in Table IX.

TABLE IX. Smoke, Fire, and Flash Points of Common Fats Containing Principally C<sub>16</sub> and C<sub>18</sub> Acids.

Free fatty acids, %	Smoke pt., °F.	Flash pt., °F.	Fire pt., °F.
0.01.....	450	625	685
0.10.....	390	620	680
1.0 .....	315	600	675
10.0 .....	240	470	550

**Thermal Conductivity.** Fats are relatively poor conductors of heat. The thermal conductivity varies little for different oils, and ranges from about 0.00040 cal./(sec.)(sq.cm.)(°C./cm.) at 20°C. to 0.00039 at 100°C. or 0.097 B.t.u./(hr.)(sq.ft.)(°F./ft.) at 68°F. to 0.095 at 212°F.

**Solubility and Miscibility.** Fats and oils are freely miscible with most organic solvents except alcohols at temperatures above their melting points. Castor oil exhibits the peculiarity of free miscibility with alcohols and limited miscibility with hydrocarbons at atmospheric temperatures. At temperatures far below their melting points, fats are only very slightly soluble in solvents.

Ordinary refined liquid oils dissolve about 0.07% of their own weight of water at -1°C. and about 0.14% at 32°C. The solubility of liquid oils in water is extremely low. Liquid oils dissolve about 92% of their own volume of carbon dioxide at 64°C. and about 62% at 140°C. The solubility of other gases, such as nitrogen, oxygen, hydrogen, and carbon monoxide *increases* with increasing temperature of the oil (3). Air dissolves in liquid oils to the extent of about 8 vol./100 vol. oil at 30°C. and 13 vol./100 vol. at 150°C. In all cases there is a linear relationship between solubility and temperature.

**Refractive Index.** The refractive index of an ordinary fat is dependent upon its average molecular weight (and to a minor degree upon its glyceride structure), as well as its degree of unsaturation, but is useful for estimating the iodine value because of the ease and rapidity with which it can be determined and because there is little variation in the average molecular weight among many common fats. Determinations of the refractive index are particularly useful in the control of fatty-oil hydrogenation.

A curve drawn through the points given in Table X will usually indicate the iodine value of an oil or hydrogenated oil such as soybean, sesame, corn, sunflower, or sardine with fair accuracy (2–3 units), provided that the oil is substantially neutral and has not suffered oxidation. In oils high in free fatty acids, the refractive index will be lower than indicated, and in oxidized oils it will be higher.

TABLE X. Iodine Value Versus Refractive Index for Common Fats and Hydrogenated Fats.

Iodine value	$n_D^{60}$	Iodine value	$n_D^{60}$
0.....	1.4468	125.....	1.4597
25.....	1.4490	150.....	1.4628
50.....	1.4512	175.....	1.4657
75.....	1.4540	200.....	1.4687
100.....	1.4568		

For oils with saponification values (average molecular weights) different from the oils mentioned above, corrections to the refractive indexes listed should be made as follows: for cottonseed oil, lard, etc., subtract 0.0005; for tallow, palm oil, etc., subtract 0.0010; for palm-kernel oil, subtract 0.0055; for coconut oil, subtract 0.0060; for rapeseed oil, add 0.0008. Castor oil and tung oil, which have fatty acids of unusual structure, have much higher refractive indexes: 1.4730–1.4750 and 1.5170–1.5200, respectively, at 25°C. (unhydrogenated oil). The refractive index decreases to the extent of about 0.00038 for each increase in temperature of 1°C.

#### REACTIONS

The reactions of fats are to a large degree reactions of the component fatty acids (*q.v.*). The autoxidation of fats and oils is a reaction of particular importance, because of its role in drying oils (*q.v.*) and in fat rancidification. In general, the readiness with which a fat undergoes oxidation is dependent upon its unsaturation. Spoilage in fat products is almost always a result of atmospheric oxidation rather than the action of microorganisms, although in fatty products of appreciable moisture content, ketonic rancidity, due to the peroxidase activity of molds, may occur. For reactions peculiar to fats, as distinguished from fatty acids, see *Ester interchange*; "Manufacture from fats" under *Fatty acids*; *Soap*.

#### Analysis and Testing

The two most important chemical characteristics of fats are the **iodine value** (the number of grams of iodine or equivalent halogen absorbed under standard conditions by 100 grams of fat), which indicates the average degree of unsaturation, and the **saponification value** (the number of milligrams of potassium hydroxide required to saponify 1 gram of fat), which is indicative of the average molecular weight. European workers commonly calculate saponification values in terms of the **saponification equivalent** (the number of grams of fat saponified by 1 mole (56.1 grams) of potassium hydroxide).

Unsaturated fatty acids absorb thiocyanogen in a manner that is different from the absorption of iodine, and different according to the number and position of the double bonds; hence, the **thiocyanogen value** (which is calculated in terms of iodine on a percentage basis under standardized conditions), taken together with the iodine value, gives an indication of the fatty acid composition of a fat (1). See also "Separation and analysis" under *Fatty acids*.

Characteristics sometimes determined in dealing with special oils include the Reichert-Meissl, Polenske, and Kirschner values, which depend upon the content of low-molecular fatty acids and hence are useful in detecting adulteration in butterfat. The **Reichert-Meissl value** is expressed as the number of milliliters of 0.1 *N* alkali required to neutralize the water-soluble volatile fatty acids (largely butyric, caproic, and caprylic) obtained from 5 grams of the fat or oil by a specified method of saponification and distillation. The value for butter is relatively high, 21-34; for coconut oil and other lauric acid oils, 3-8; and for most other edible fats and oils, less than 1. Similarly, the **Polenske value** is a measure of water-insoluble volatile fatty acids (largely capric and lauric). The value for butter is 1.5-3 and for coconut oil, 15-18. The **Kirschner value** indicates the content of water-soluble volatile fatty acids having soluble silver salts (butyric acid). For special oils, such as castor oil, a measure of the free hydroxyl groups is the **acetyl value**, the number of milligrams of potassium hydroxide required to neutralize the acetic acid produced by hydrolysis of 1 gram of acetylated fat.

Determinations are often made of the percentage of **unsaponifiable matter**, those components that do not form sodium or potassium soaps, but are soluble in the common oil solvents. In most refined fats, the content of unsaponifiable matter (largely sterols) is 0.5-1.0%, although in high-grade animal fats and coconut oil and other lauric acid oils it is often lower, and in a few fats (for example, rice-bran oil and shea fat) it may be substantially higher. Determinations are also often made of the percentage of **free fatty acids**, which is calculated as lauric acid for coconut and palm-kernel oils and as oleic acid for most other oils. The free fatty acids can also be expressed in terms of the **acid value**, the number of milligrams of potassium hydroxide required to neutralize the free fatty acids in 1 gram of fat. The relationship between acid value and per cent free fatty acids (calculated as oleic acid) is: 1 unit of acid value = 0.503% free fatty acids.

A number of color tests are used for the detection of specific oils in mixtures, of which only the Halphen test for cottonseed, kapok, or baobab oil and the Baudouin or Villavecchia test for sesame oil are altogether reliable. The **Halphen test** depends upon the development of a rich red color when cottonseed oil (or kapok or baobab oil) is heated with amyl alcohol and carbon disulfide containing 1% of sulfur. The reaction is ineffective if the cottonseed oil has been hydrogenated to any considerable degree; however, unhydrogenated oil can be detected if only 1% is present in a mixture of oils. The **Baudouin test** depends upon the development of a persistent rose-red color when sesame oil or hydrogenated sesame oil is treated with a mixture of concentrated hydrochloric acid and cane sugar; it will detect 2% of sesame oil. The **Villavecchia test**, a modification of the Baudouin test, uses furfural instead of cane sugar.

The resistance of a fat to atmospheric oxidation is usually determined by subjecting samples to conditions that greatly accelerate their normal course of oxidation, and noting the time required for a specific high peroxide value (corresponding to rancidity or near-rancidity) to develop. Standard methods include the **A.O.M.** or **Swift stabil-**

**ity test** (aeration test) (28,34) in which the samples are aerated at 97.7°C. or, in a modification of this test, at 110°C. and the values (times) are reported in hours, and the **Schaal or oven test** (24) in which the samples are incubated in an oven at 60°C. and the values are reported in days. Some laboratories determine the stability of a fat by measuring the time required for it to absorb a specific volume of oxygen at an elevated temperature (15a). Where some degree of oxidation has occurred before testing the fat, a determination of the **peroxide value** is usually depended upon to evaluate the extent of oxidation. The peroxide value is a determination of the ability of compounds produced by oxidation to liberate iodine from potassium iodide in glacial acetic acid and is expressed in terms of millimoles of peroxide or milliequivalents of oxygen per 1000 grams of fat. There are a number of tests for advanced deterioration or incipient rancidity based upon the presence of aldehydes, of which the **Kreis test** (development of a red color with hydrochloric acid and phloroglucinol) is perhaps the best known. A qualitative test for aldehydes that can also be used is the **Schiff test**, which depends upon the formation of a violet-red color when aldehydes are treated with Schiff reagent (a solution of fuchsin that has been decolorized by passing sulfur dioxide through the solution).

In dealing with hydrogenated oils, **nickel**, which may be present as an impurity, is sometimes determined.

For special tests applied in the grading of oils for trading purposes, including refining tests and tests for evaluation of oils on the basis of their depth of color, see *Cottonseed*; *Soybeans*. The physical characteristics of importance in the analysis and testing of fats are discussed under "Physical and thermal properties." As sources of detailed information on analytical and testing methods, the publications of the American Oil Chemists' Society (1) and Jamieson (22) are recommended. See also *Fatty acids*; *Food analysis*.

### Extraction of Fats and Oils

The commercially important oil-bearing materials include oilseeds, the pulp of certain fruits, and fatty animal tissues. In oilseeds, the oil is concentrated in the kernel, which may contain as little as 16–20% oil in the case of soybeans, or as much as 65–70% oil in the case of copra or babassu kernels. The important oil-bearing fruits are the olive and the oil palm, the pulp of which contain about 25–35% oil and 40–50% oil, respectively. The fat content of fatty animal tissues ranges usually from about 60 to 90%. Fat from land animals, such as cattle, sheep, and hogs, and from the whale, is recovered largely from fatty tissues that have been trimmed from other portions of the carcass, but fish oils are usually obtained by processing whole animals that contain 10–20% oil. Residues from the processing of oilseeds or animal tissues for oil recovery are high in protein content, and are widely used as animal feeds (see *Feeds, animal*). In the U.S., cottonseed, soybean, linseed, peanut, copra, and fish meals or "cake" and animal "tankage" are in particular important articles of commerce, which are sold at prices based principally upon their protein content. Certain of the residues find some use as plant foods or fertilizers, and there is a limited use of certain oilseed residues (principally soybean) as a source of human food or industrial protein products.

Methods for the recovery of fat or oil from oilseeds or other oil-bearing materials will be treated in more detail in special articles dealing with individual fats (see *Cottonseed*; *Fish*; *Fish-liver oils*; *Meat and meat products*; *Soybeans*).

Oil-bearing materials that are to be extracted are first pretreated mechanically to facilitate the separation of the oils from the solids. These pretreatments include cleaning, decortication (for large oilseeds), and size reduction or crushing (for almost all oil-bearing materials).

Except in the recovery of olive oil and a small quantity of "cold-pressed" oil from oilseeds, the mechanical expression of oil-bearing materials is invariably preceded by heat treatment, to coagulate proteins and make the parent material permeable to oil flow, to decrease the affinity of the oil for the tissue solids, to cause coalescence of small oil droplets, and to increase the fluidity of the oil. While in the case of oilseeds, such treatment (called cooking) is purely a preparatory operation, in the case of animal tissues, separation of the oil is largely accomplished during the course of the heat treatment (called dry or wet rendering).

Mechanical expression (by batch pressing, continuous pressing, or centrifugal expression) is utilized to recover the major portion of the oil from many oilseeds with a high oil content and from fruit pulp. It is also utilized to recover oil from rendering residues. For maximum recovery of the oil from oilseeds with a low oil content, solvent extraction (batch or continuous) is more efficient than mechanical expression; recently, it has also been used for a few oilseeds of high oil content. Solvent extraction is also utilized for final recovery of oil from residue from mechanical expression. See *Centrifugal separation*; *Extraction*.

#### PROCESSING OF OLSEEDS

**Mechanical pretreatment** of oilseeds includes: cleaning to remove foreign material; decortication, in the case of the larger oilseeds; and reduction of the kernels. Representative practices applicable to most oilseeds are described in detail in the articles on *Cottonseed* and *Soybeans*. Special *decortication* methods are required for large oilseeds with thick hulls, such as coconuts and palm nuts. Coconuts are split and dried either by exposure to the sun or by forced heating, to detach the hulls and produce the copra of commerce. The preliminary decortication and drying of coconuts and the various palm nuts is carried out in the producing regions, often by hand labor. Other oilseeds are generally shipped in an undecorticated form and processed all together at the oil mills.

*Reduction* of oilseeds to relatively small particles or to thin flakes is a necessary preliminary to oil recovery by any means. Reduction methods for small oilseeds are described in connection with the processing of cottonseed and soybeans. In the processing of copra or other large oilseeds, preliminary reduction is often accomplished by the use of hammer mills.

**Cooking** of oilseeds before mechanical pressing is essentially the same for other oilseeds as for cottonseed (*q.v.*) and soybeans (*q.v.*). Somewhat different practices are followed according to whether the seeds are to be hydraulically pressed or pressed in continuous screw presses. As considerable mechanical heat is generated in the latter, less preliminary heat treatment is required. An important part of the cooking operation is adjustment of the moisture content, to give the seed mass the proper plasticity for efficient pressing. Castor beans are virtually the only oilseed pressed in quantity in the U.S. without preliminary heat treatment (see *Castor oil*).

Details of the **mechanical expression** of oilseeds, by means of *open hydraulic presses* or *continuous expellers* or *screw presses* (see *Presses*), are to be found in the articles on *Cottonseed* and *Soybeans*. The *cage press*, which consists of a vertical per-

forated cage in which oil is expelled from the seed by the action of a ram, has been little used in the U.S. except for the cold pressing of castor beans and the processing of copra, and for the latter it is now largely replaced by the screw press. Although relatively expensive and cumbersome in operation, it has the advantage of requiring no press cloths, and of being able to handle high-oil materials, which are difficult to retain in cloths. As it permits the generation of very high pressures (5000–6000 p.s.i.), it is particularly suitable for pressing uncooked seeds. The *pot press*, a steam-heated modification of the cage press, with multiple cages or pots, and bottom rather than side drainage, is widely used for the processing of cocoa beans or other oilseeds containing a fat of high melting point (see Vol. 3, p. 903).

In Europe, pressing, either continuous or discontinuous, is often conducted in successive stages at increasingly higher pressures, but this practice is uncommon in the U.S.

**Solvent extraction** is a highly efficient means of oil recovery, which is capable of reducing the oil content of oilseed residues to about 0.5%, as compared with 4–6% by mechanical expression. It is particularly advantageous in the processing of seeds of low oil content, and for this reason has in the past found application in the U.S. principally in the soybean industry. Recently, however, it has been extended to the processing of other oilseeds, including cottonseed (*q.v.*), flaxseed, and corn germs. As solvent extraction becomes mechanically complicated in proportion to the oil content of the seed (high-oil seeds tend to disintegrate during extraction), it is common practice to “pre-press” seeds of high oil content in low-pressure screw presses (to about 10% residual oil) before extraction.

The design and operation of the continuous extractors used in all large plants are described in connection with the processing of soybeans (*q.v.*). Batch extractors are used to a considerable extent for the extraction of castor bean pomace or residue from mechanical expression. The usual solvents are a light petroleum fraction (so-called extraction naphthas) such as a grade consisting chiefly of *n*-hexane.

#### RECOVERY OF OIL FROM FRUIT PULPS

**Olives**, after being crushed in edge-runner or other types of mills, are pressed in open hydraulic presses, or, occasionally, pot presses or screw presses. In European practice, relatively low-pressure (500–1000 p.s.i.) open presses are used, and pressing is conducted in two or three stages, with segregation of the oil from each stage. The product of the first pressing is so-called “virgin” olive oil. Separation of oil from the aqueous material that is expressed is carried out by prolonged settling. As olive oil is relatively expensive, the residue or “marc” from pressing, which contains 8–10% oil, is commonly solvent-extracted with a hydrocarbon solvent to produce an oil that is salable as an edible oil after refining. So-called “sulfur olive oil,” obtained by solvent extraction with carbon disulfide according to older European practice, is not edible.

Bunches of **palm** fruits are first “sterilized,” to stop enzyme action and loosen the fruit from the stalks, by a short steam treatment in an autoclave. The fruits are then stripped off and cooked or “digested” in open steam-heated kettles. The digested and partially dried material is pressed in special steam-heated cage presses, and, after the addition of water, the extract is separated into an oil layer and a water and solids layer by settling or centrifuging. By an alternative method, dehydration of the fruits during sterilization and digestion is avoided, and the oil is separated in an atmos-

phere of steam in a basket centrifuge. The two methods are said to be equally efficient.

#### RENDERING OF ANIMAL FATS

The wet-rendering and dry-rendering methods used in U.S. packing houses for the recovery of lard, tallow, and greases are described in connection with *Meat and meat products*. Rendering methods for other animal fats, including marine oils, are essentially similar (see *Fish-liver oils*); however, whale and fish oils are invariably wet-rendered, often continuously, with centrifugal separation of the fatty and aqueous phases. Open hydraulic presses, cage presses, and continuous screw presses are all used for the final recovery of oil from rendering residues, and the latter are often solvent-extracted after pressing.

#### Processing

The following discussion of oil processing will cover only those methods that are applied to fats and oils generally, and will exclude special methods for individual products (see *Driers and metallic soaps*; *Drying oils*; "Manufacture from fats" under *Fatty acids*; *Margarine*; *Paint*; *Salad dressings*; *Shortenings*; *Soap*; etc.). Castor, olive, fish, sperm, linseed, soybean, and rapeseed oils are now sulfated or sulfonated for use as textile assistants, leather-filling agents, cutting oils, etc. (see *Castor oil*; *Sulfonic acids*; *Surface-active materials*; *Textile assistants*; etc.).

#### REFINING

Crude fats or oils are refined to remove free fatty acids and phosphatides and other gummy or mucilaginous materials and to improve the color.

**Alkali Refining.** Refining is generally carried out by treating the fat with a strong (10–20°Bé.) solution of caustic soda. The process involves: (1) emulsifying the fat with a considerable excess of the aqueous alkali solution, (2) heating to break the emulsion, and (3) separating the refined oil from the precipitated soap and miscellaneous associated impurities. The precipitated material, known in the trade as "foots" or "soapstock," is a commodity that usually contains 30–50% free and combined fatty acids; this commodity, with or without acidulation to decompose the soap and remove excess water, is sold for use in soapmaking and the manufacture of commercial fatty acids.

By means of refining, crude oils, which seldom contain less than 0.5% free fatty acids and often contain much more, are reduced to a free fatty acids content of 0.01–0.03%.

*Batch caustic soda refining* is carried out in open kettles equipped with cone bottoms, heating coils, and variable-speed mechanical agitators, in which separation of the refined oil and soapstock is effected by prolonged gravity settling. In the batch refining of animal fats and vegetable fats of the lauric acid type, which are almost free of phosphatides, relatively little neutral oil is lost by saponification or occlusion in the soapstock. However, in refining vegetable oils such as cottonseed and soybean, the presence of phosphatides or other surface-active materials leads to considerable neutral-oil losses. Cottonseed oil, for example, which contains 1.0% free fatty acids and 2.0% phosphatides and other nonglyceride impurities, will often have a refining loss by the batch method as high as 7–8%. Consequently, there has been widespread

adoption, particularly in the U.S., where cottonseed and soybean oil processing predominate, of a *continuous caustic soda refining process* (21,37,42,43), which reduces the refining loss (usually by 25–30%) by shortening the contact time between caustic and oil, and by separating the oil and soapstock very efficiently in high-speed centrifuges. Continuous caustic soda refining was introduced in the U.S. in about 1933, and in succeeding years largely replaced batch refining for the treatment of vegetable oils.

More recently, the continuous caustic soda refining process has, in turn, been supplanted in some refineries by the *Clayton continuous soda ash-caustic soda process* (33,37,44). The Clayton process (Fig. 3) is essentially similar to the continuous caustic soda process, except that refining is carried out in two stages and with two reagents. In the first stage, the oil is largely neutralized, and phosphatides and other gums are removed by treatment with a 20°Bé. soda ash solution; in the second stage, neutralization is completed, and color bodies are taken out by treatment with 20°Bé. caustic soda solution. A dehydration step is required after the soda ash treatment to

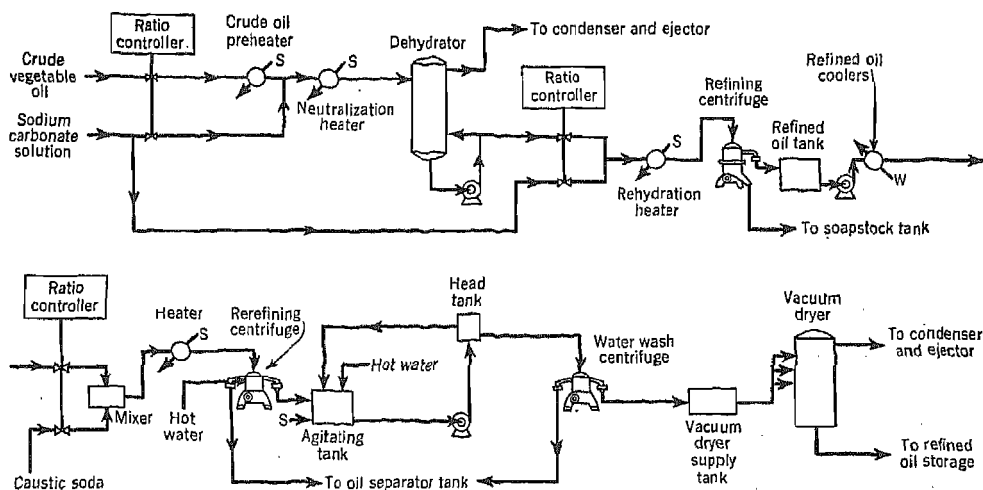


Fig. 3. Flow diagram, Clayton continuous soda ash-caustic soda refining process.

remove entrained carbon dioxide from the soapstock; the soapstock must then be rehydrated (with soda ash solution) to enable it to discharge freely from the first-stage centrifuges. In both the caustic soda and the soda ash-caustic soda systems, continuous water-washing and vacuum-drying equipment is incorporated to permit the plant to deliver a dry and substantially soap-free refined oil.

Oils can generally be refined by the soda ash-caustic soda method with a loss only slightly (0.2–0.8%) in excess of the so-called "Wesson loss"; the latter represents substantially the content of substances other than glycerides in the oil, and hence the theoretical minimum to which the refining loss can be reduced. This usually corresponds to a saving in refining loss of 40–50% as compared with batch refining.

Basic patents on both continuous refining systems are held by Refining, Inc.; the Sharples Corporation and the DeLaval Company supply plants differing in certain details.

*Hydration* or "degumming" of crude vegetable oils with water or a weak aqueous



solution to precipitate phosphatides, is often practiced before alkali refining, particularly in dealing with solvent-extracted soybean oil, where the phosphatides or gums form the raw material for the production of commercial lecithin (*q.v.*). Hydration is usually carried out continuously, with separation of the gums being effected in high-speed centrifuges.

**Acid Refining.** Drying oils intended for technical use are sometimes acid-refined, that is, treated with a small amount of strong (about 60°Bé.) sulfuric acid, to char and precipitate phosphatides and similar impurities.

**Steam Refining.** Lard or other high-grade animal fats and vegetable oils substantially free of phosphatides can be successfully steam-refined or deacidified by steam stripping at high temperatures under a vacuum.

**Solvent Refining.** The Solexol process of liquid-liquid extraction with propane (see *Extraction*) is very effective for the removal of color bodies from low-grade fats, and is used to some extent for refining inedible tallows and greases for soapmaking.

#### BLEACHING OR DECOLORIZATION

For many products, including shortening, margarine, high-grade soaps, and light varnishes and enamels, alkali refining alone does not produce a sufficiently light-colored oil, and additional bleaching treatment is required.

**Adsorption.** Bleaching is usually effected by treating the refined oil with an absorbent in powder form. Both natural (fuller's earth) and acid-activated bleaching earths (or clays (*q.v.*)) are used as adsorbents. The latter are more expensive, but have greater adsorptive power for fat pigments, particularly for chlorophyll or related compounds. Activated carbon is used in bleaching to some extent, but usually only as an adjunct to a bleaching earth, and in much smaller quantity; it tends to take up impurities as well as pigments, including traces of soap left from refining (see Vol. 2, p. 883).

Bleaching is usually carried out at a temperature of 220–240°F. (104–116°C.) under atmospheric pressure; in bleaching under vacuum, slightly lower temperatures may be employed. More than about 1% of activated earth is seldom used in bleaching good edible oils, although considerably more may be required if a natural earth of lower activity is used or if the oil is of poor grade and highly colored. Equilibrium between unadsorbed pigments in the oil and adsorbed pigments on the earth is quickly established (within about 5 minutes) when the latter is vigorously agitated with the oil. In the common practice of batch bleaching, the oil and adsorbent are heated and mixed together in a kettle of about 30,000-lb. capacity, after which the kettle charge is pumped through a filter press. The press cake of spent adsorbent is blown with air, or steam and air, to reduce its entrained oil content to a minimum of 30–40% and is discarded, in some cases after solvent extraction or other treatment for further oil recovery.

To avoid oxidation, which is injurious to the stability of the oil and also, in the case of vegetable oils, to bleaching efficiency, the operation is preferably carried out in a closed kettle under vacuum, although the use of open kettles is not uncommon. Continuous closed bleaching systems, in which the oil or oil-earth slurry is sprayed into an evacuated chamber for deaeration, are used to some extent (9,27,47).

**Chemical bleaching methods** (using such reagents as sodium dichromate or chlorine dioxide) depend upon the oxidation of fat pigments to colorless forms. As they involve hazard of oxidation of the oil also, they are not used in processing edible fats,

and are applied on but a limited scale in the treatment of fats for technical use. The Soloxol process of extraction with liquid propane (see *Extraction*) constitutes an effective bleaching method, particularly for fats that contain pigments difficult to remove by adsorption. A considerable bleaching effect (principally through the reduction or heat destruction of carotenoid pigments) is incidental to the hydrogenation process, and also, to a lesser degree, to steam deodorization or other heat treatment of vegetable oils.

#### HYDROGENATION

Hydrogenation is a highly important process of the fatty-oil industry, particularly in the manufacture of edible fat products (see *Margarine*; *Shortenings*), where it is used to convert liquid oils such as cottonseed and soybean oils to plastic fats, and also of soaps (*q.v.*). In addition to its effect upon the melting point and consistency of oils and fats, hydrogenation improves the resistance of the edible fat products to atmospheric oxidation. The stability of a partially hydrogenated fat depends principally upon its decreased content of linoleic or other polyunsaturated acids, as these acids oxidize much more readily than oleic acid (16,17). As defined here, hydrogenation refers to the reduction of ethylenic linkages in fatty acid chains; for hydrogenation at the carboxyl group to produce fatty alcohols, see Vol. 1, pp. 313, 318, 319, 320; *Fatty acids*. See also *Hydrogenation*.

As carried out commercially, the hydrogenation of fats, fatty acids, or other fatty esters is a liquid-phase process in which gaseous hydrogen is dispersed and caused to dissolve in the heated fat, where, under the influence of a solid catalyst (almost invariably nickel), it combines with unsaturated fatty acid radicals. Although continuous hydrogenation with a fixed catalyst has been practiced on a limited scale (11), the process has inherent disadvantages, and virtually all present-day hydrogenation is carried out batchwise with a powder catalyst, which is removed from the fat by filtration at the conclusion of the reaction and is generally re-used a number of times. The rate of reaction, as well as the course of the reaction and the composition of the hydrogenated product, is profoundly influenced by the nature of the catalyst and also the conditions under which hydrogenation is conducted, including the temperature, pressure, thoroughness of dispersion of hydrogen in the oil, and catalyst concentration. The present process is not essentially different from that originated by Normann (40) and placed in large-scale operation in the period about 1905–1915; improvements in hydrogenation practice have resulted chiefly from the development of improved catalysts and more efficient methods of dispersing the hydrogen in the oil, and better understanding of the effects of the different operating variables.

**Principles.** The typical effect of hydrogenation on the composition of an oleic–linoleic acid oil is illustrated in Figure 4. Hydrogen absorbed by the oil is used principally in converting linoleic acid to oleic acid, rather than in converting oleic acid to the saturated (stearic) acid. However, the oleic acid formed during the course of hydrogenation is not wholly normal oleic acid (*cis*-9-octadecenoic acid), but consists in part of trans forms of oleic acid and its isomers. As these so-called “isooleic” acids are higher melting than the normal acid, the consistency and melting point of the hydrogenated fat depend to a considerable degree upon the extent to which they are formed, as well as the degree to which linoleic acid is hydrogenated, in preference to oleic acid. In general, isooleic acids increase the hardness of the fat at lower temperatures (up to about 35°C.) but have relatively little effect upon the consistency at higher

temperatures (35–45°C.), whereas saturated acids formed during the reaction contribute to the consistency in both ranges of temperature (5). The technology of fat hydrogenation (for the manufacture of margarine and shortening) is largely concerned with control of the reaction to provide the proportions of saturated, isooleic, normal oleic, and linoleic acids that are required to provide specific consistency and stability characteristics in the hydrogenated products.

The term *selectivity* is applied in reference to the preferential hydrogenation of linoleic acid in fats where both linoleic and oleic acids are present. In general, selectivity is associated with the formation of relatively large amounts of isooleic acids, and is promoted by a high temperature, a high catalyst concentration, a low hydrogen pressure, and a low degree of hydrogen dispersion in the oil. It appears that the factors of catalyst concentration, pressure, and hydrogen dispersion, and possibly also temperature, all affect the selectivity through their influence upon the concentration

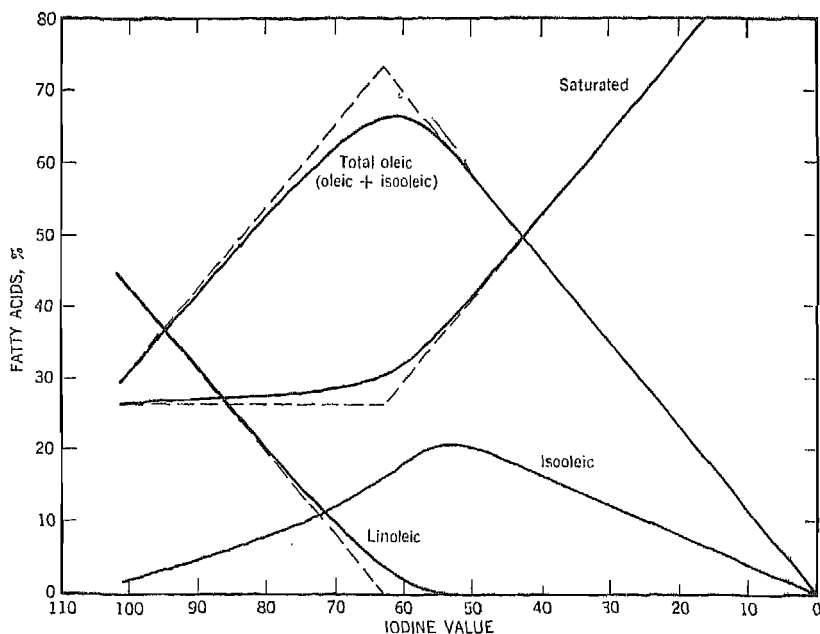


Fig. 4. Effect of hydrogenation on the composition of cottonseed oil. (Broken lines represent theoretical contents of saturated, oleic, and linoleic acids with complete selectivity of hydrogenation.)

of hydrogen in the reaction zone (that is, adsorbed on the catalyst), with selectivity being favored by a low concentration (6). With very high selectivity, the rate at which hydrogen reacts with linoleic acid may be as much as 50 times as great as its rate of reaction with oleic acid; under conditions leading to very low selectivity, the reaction rate of linoleic acid may be no more than 4 times that of oleic acid (6). In the hydrogenation of cottonseed oil, the isooleic acid content (as determined by the usual lead soap-alcohol method) may rise to a maximum as high as 25–30% with very selective hydrogenation, or as low as 3–4% with very nonselective hydrogenation.

Selectivity appears to be largely a matter of a difference in reactivity between double bonds separated by an active methylene group (as in linoleic acid) and double

bonds more widely separated (19); hence, if the double bonds are widely separated, polyethenoid acids are not highly reactive. Furthermore, as the number of double bonds in a fatty acid is increased beyond two, further increase in reactivity is not comparable to the difference between linoleic and oleic acids. An "isolinoic" acid (9,15-octadecadienoic acid), for example, hydrogenates only about 2.5–4.0 times as readily as oleic acid, and linolenic acid only about 1.5–2.5 times as readily as linoleic acid, with the exact ratio in each case being relatively little dependent upon hydrogenation conditions (6).

Different catalysts vary considerably with respect to the amount of isooleic acids produced at a given level of saturated acid formation. In the industry, catalysts that tend to suppress the formation of *both* saturated and isooleic acids are termed *selective*.

**Hydrogenation Reactors.** The reactors in common use in the U.S. are of two types. The *hydrogen-recirculation type* consists of a tall cylindrical vessel that often has no mechanical agitator, but is provided with a hydrogen distributor in the bottom

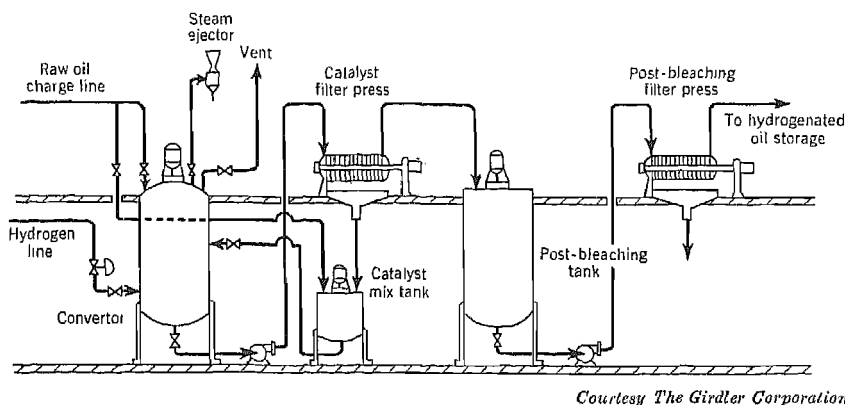


Fig. 5. Simplified flow diagram of hydrogenation plant, dead-end system.

through which hydrogen in excess of the amount required for reaction is blown during the course of reaction; the hydrogen not absorbed is recirculated from the headspace by means of a blower. The vessel is usually designed for pressures only slightly in excess of atmospheric, and is supplied with hydrogen from a low-pressure holder. Internal steam and water coils are provided for heating the charge of oil and catalyst and for carrying away the heat of reaction, but the finished batch is usually cooled by pumping it out through an external heat exchanger, as agitation within the vessel ceases when hydrogen flow is stopped at the conclusion of the reaction.

The newer *dead-end system* employs a vertical, cylindrical, pressure vessel with a mechanical agitator of the gas-dispersion type, and is supplied from high-pressure storage tanks with only as much hydrogen as is absorbed by the oil. It is provided with internal coils for both heating and cooling, and often with a steam ejector for maintaining the vessel under vacuum during periods when hydrogenation is not progressing. The recirculation reactor is kept filled with hydrogen at all times. A complete hydrogenation plant employing the dead-end system is illustrated in Figure 5.

There is no great difference between the two systems with respect to the reaction rate, and preference for one or the other is based upon consideration of such factors

as installed cost, operating economy, and ease of hydrogenation control. The usual range of capacities for either is 10,000–40,000 lb. per batch.

In practice, hydrogenation is usually carried out with maximum hydrogen dispersion and a fairly constant concentration of catalyst (0.05–0.15% nickel), and adjustments of the temperature and pressure are depended upon to give the variations in selectivity that are required for different products. The usual ranges of temperature and pressure are about 250–375°F. (120–190°C.) and 0–100 p.s.i.g., respectively. In general, margarine oils are hydrogenated very selectively at relatively low pressures and high temperatures, to produce a firm but low-melting product, whereas shortening stocks are hydrogenated with moderate selectivity at lower temperatures and higher pressures, to obtain the minimum iodine value and maximum stability consistent with proper low- and high-temperature consistency. In the hydrogenation of edible hard stocks for blending with soft oils, or in the hydrogenation of inedible fats for manufacture of fatty acids such as stearic acid or for soapmaking, the selectivity of the reaction is unimportant; thus, a combination of high temperature and high pressure is used to make the reaction as rapid as possible. Margarine or shortening stocks are generally hydrogenated within 1–2 hours. A somewhat longer time is usually required for the hydrogenation of hard stocks or inedible fats.

**Catalysts** for hydrogenation are prepared by the “wet reduction” or thermal decomposition of nickel formate or other heat-labile nickel salt in a fatty oil at about 425–450°F. (218–232°C.), or by the “dry reduction” with hydrogen of nickel carbonate or nickel hydroxide precipitated on a diatomaceous earth carrier at about 800–900°F. (427–482°C.). Wet-reduced catalysts are often copper-promoted to facilitate reduction (41); the promotion of nickel catalysts with other metals is uncommon. There is a limited use of catalysts of the Raney or nickel alloy type. Platinum and palladium are effective hydrogenation catalysts, but offer no advantages over the much cheaper nickel, and hence find no commercial use. The most desirable catalysts are highly active, as selective as they can be made without undue sacrifice of ruggedness or activity, and uniform with respect to both activity and selectivity. A large part of the catalysts consumed in the U.S. is now made by chemical companies specializing in catalyst manufacture, rather than by oil processors.

Catalysts are readily inactivated or rendered nonselective by a variety of poisons, which may be present in either the oil or the hydrogen. The oil to be hydrogenated must be free of phosphatides or other gums, and also soap and sulfur or halogen compounds. The common gaseous catalyst poisons, from which the hydrogen must be rigorously purified, include sulfur compounds (hydrogen sulfide, carbon disulfide, organic sulfur compounds) and carbon monoxide. Poisoning of the catalyst with carbon monoxide has the peculiarity of being reversible when the catalyst–oil mixture is subjected to reduced pressure, and of being most pronounced at the lower hydrogenation temperatures. Carbon dioxide, nitrogen, methane, and water vapor are not catalyst poisons, although they may be undesirable hydrogen diluents.

#### DEODORIZATION

With the exception of olive oil, which is prized for its natural flavor and odor, virtually all of the vegetable oil entering edible fat products in Occidental countries is subjected to deodorizing treatment for flavor and odor removal. Although lard is largely consumed in its natural form, there is now a significant and growing produc-

tion of deodorized lard products in the U.S., and the considerable amount of lard and edible tallow incorporated into compound-type shortenings is also deodorized. All hydrogenated fats intended for edible use must be deodorized to free them of the typical flavor and odor imparted by hydrogenation.

The identity and concentrations of the odoriferous materials in fats and oils have never been established satisfactorily, although it is known that they include ketones and terpenes (23), and that they generally constitute less than 0.1% of the total weight of the oil.

Deodorization is a process of steam distillation, in which the relatively nonvolatile oil is maintained at a high temperature and under reduced pressure while it is stripped of the relatively volatile constituents responsible for flavor and odor. Free fatty acids in the oil are usually reduced to 0.01–0.03% if originally present in greater amount, and vegetable oils and their products also ordinarily undergo a considerable reduction in color. In the manufacture of edible products, deodorization is almost invariably the last step in processing before finishing and packaging.

Rather drastic treatment is required to produce the completely bland and odorless fats that are demanded by consumers in the U.S. and in many sections abroad. Even at elevated temperatures and low pressures, prolonged stripping, with a considerable quantity of steam, is required for satisfactory flavor and odor removal. In modern installations, three-stage steam ejectors with barometric intercondensers are usually used for maintaining a vacuum on the oil; with these, depending upon the temperature of the condenser water, 3–4 lb. of motive steam is required for each pound of steam used for stripping. Hence steam requirements of the process are relatively high. As the volatility of the odoriferous components of an oil appears to increase with increase in the temperature at roughly the same rate as the vapor pressures of the common fatty acids (doubling with each increment of about 30°F. (17°C.)), and as stripping-steam requirements at a fixed temperature are in direct proportion to the absolute pressure (2), the importance of high temperature and high vacuum in the interest of steam economy is manifest. Modern developments in deodorization have been primarily a matter of working toward higher vacuums and, more particularly, higher temperatures, which are now generally in the range of 425–475°F. (218–246°C.), and at the same time effecting mechanical improvements in the equipment. The effective use of higher temperatures has made mechanical design more exacting, as the deleterious effect of accidental air leakage is greatly magnified, as is also that of metallic contamination of the oil. In modern deodorizing practice, the rigorous exclusion of oxygen from the oil in process may be regarded as absolutely essential.

The common **batch deodorizer** is a vertical cylindrical vessel, usually designed to hold 20,000–30,000 lb. of oil. To accommodate rolling and splashing of the oil charge without excessive carry-over, a headspace approximately equivalent to the depth of oil is usually provided. Stripping steam at the rate of about 500–1000 lb. per hour is injected into a distributor at the bottom of the vessel and, after passing upward through the oil, is taken off at the top through a large vapor line communicating with the ejector system. Most modern installations operate at an absolute pressure of 5–6 mm., which is the practical limit of three-stage steam-ejector equipment. A few four-stage ejector systems are in operation that produce a pressure of 1–2 mm., but it is generally considered that the advantages gained with the lower pressure are not commensurate with the increased motive-steam consumption.

Practice varies in heating and cooling the oil charge. Some deodorizers contain no heating or cooling coils; the charge is heated before deodorization by recirculation through an external heater, and is pumped out through a cooler after it is deodorized. In other installations, the oil is heated in the deodorizer, and cooled externally; in still others, internal coils are provided for both heating and cooling. In any case, it is necessary to reduce the temperature of the oil to 120–140°F. (49–60°C.) before it is exposed to the atmosphere to avoid injury to its flavor or flavor stability. Some processors withdraw deodorized shortening under nitrogen and likewise plasticize and package under nitrogen.

Batch deodorizers are generally built of ordinary carbon steel, although recently increasing use has been made of nickel or stainless steel. In laboratory tests, Ziels and Schmidt (39) have demonstrated that at deodorizing temperatures nickel and aluminum are the only common metals of construction that are completely free of pro-oxidant effect on oils. The refluxing of easily condensable materials from the cool surfaces of the upper shell and vapor lines is a source of considerable trouble in batch deodorizers. To prevent refluxing, these are sometimes provided with a heating jacket (46).

For rapid and efficient deodorization, somewhat higher temperatures are required than are obtainable with steam at ordinary boiler pressures. In the older high-temperature deodorization plants, the oil was heated by circulation through a direct-fired heater (the Wesson system), or by the circulation of mineral oil through a similar heater and then through coils in the deodorizer (the Merrill system). Some modern installations have employed high-pressure steam for heating, but preference has generally been given to the use of Dowtherm (diphenyl–diphenyl oxide) vaporizers (see *Heat transfer*), which provide sufficiently high vapor temperatures at pressures of 10–20 p.s.i.g.

In batch deodorization, stripping is carried out for periods ranging from about 2 to 10 hours; the total weight of stripping steam used per 100 lb. oil usually ranges from about 15 to 50 lb., with an average of perhaps 25 lb.

Two types of **continuous deodorizers** have found considerable use in the U.S. The first of these, the *Foster-Wheeler deodorizer* (12,15,45), introduced in about 1936, employs a stainless-steel tower with trays and bubble caps, down which deaerated oil, after heat exchange with hot effluent oil and Dowtherm vapors, is passed in counter-current flow to stripping steam. The usual amount of stripping steam used is 10 lb. per 100 lb. oil. Capacities of standard units are 2500 and 5000 lb. per hour. A number of units are in operation in the U.S. and in South America.

The second type, the *Votator "semicontinuous" deodorizer*, of The Girdler Corporation (4) employs a series of superimposed shallow nickel trays (interconnected with drop lines and automatically operated drop valves), which are suspended inside a tall cylindrical shell, and in which the oil is heated (with steam and Dowtherm vapor), stripped, and cooled, as it drops intermittently from one tray to another. The shell and tray construction provides a double wall between the oil and the atmosphere that renders it impossible for air accidentally leaking into the apparatus to come into contact with the hot oil. The oil is deodorized for 1 hour, and stripping steam requirements are 4.5 lb. per 100 lb. oil. The capacities of standard units are 2000, 5000, and 7500 lb. per hour. Introduced in 1948, it has been adopted by a number of U.S. and Canadian processors.

### Sources and Production

The sources and approximate world production of the commercially important vegetable oils are given in Table III (p. 147). Unless otherwise indicated, the plants from which the oils are obtained are cultivated or processed primarily for the oils. The most important fat derived from land animals is butterfat from cows' milk (see *Dairy products*), which is normally produced to the extent of probably at least 8 billion pounds annually, and thus, from the standpoint of volume as well as value, far outranks any other single fat or oil. The most important producing regions are the U.S., Australia, New Zealand, and western Europe. There is a very minor production of goat butterfat and of fat from the milk of the Indian buffalo (used in the manufacture of ghee). Next in point of volume are lard and tallow (see under *Meat and meat products*). The largest lard-producing sections of the world are essentially those in which quantities of corn are available for hog feeding, and include particularly the U.S. and the Danube Valley. However, there is some lard produced over most of Europe and America, as well as portions of Asia and Africa. World production amounts normally to 4 to 5 billion pounds annually. Beef and mutton tallow production, which is concentrated in the U.S., South America, Australia, and New Zealand, amounts normally to perhaps 3 to 4 billion pounds annually. A considerable proportion of the fat derived from domestic animals is not a product of factories, but is produced and consumed on the farm.

Before 1938, the annual world production of whale oil amounted to well over a billion pounds annually, of which the greater part was from whales taken in the Antarctic region by vessels of Norwegian and United Kingdom registry. There is a minor production of seal oil. Most fish oil is derived from small fishes, which, like whales, are taken primarily for their oil; of these, the California sardine (*Sardinops caerulea*, known in Canada as the pilchard), the Japanese sardine (*Clupanodon melanostica*), the menhaden, and the herring are the most important. The large producers of fish oils are the U.S., Japan, Canada, and Norway and other Scandinavian countries; the annual production is somewhat variable, but amounts to several hundred million pounds.

The production of fish-liver oils (*q.v.*), of which cod-liver oil is the most plentiful, is not large, but is important because of the vitamin content of the oils. The largest producers are the U.S., Canada, and Norway.

### Economic Aspects

The factory consumption of the principal fats and oils in different classes of products in the U.S. in 1947 is shown in Table XI. In addition to the amounts listed in the table, an estimated 1,813 million pounds of lard was consumed as such, as well as 1,606 million pounds of butter (containing about 80% fat). Normally, the only oil or fat exported in volume from the U.S. is lard. Exports varied generally from 200 to 500 million pounds in the period 1937-1947; previously, they were as high as 1,060 million pounds (in 1923), and as low as 97 million pounds (in 1935). The U.S. is partially dependent upon imports for linseed oil (principally from Argentina); largely dependent upon imports for tung oil (from China); and entirely dependent upon imports for palm oil (from Africa, British Malaya, and Indonesia), coconut oil (principally from the Philippines), and castor oil (principally from Brazil). Castor oil and coconut oil enter the U.S. largely in the form of oilseeds (castor beans and copra).



TABLE XI. Factory Consumption of Fats and Oils in Different Classes of Products in the U.S., 1947.<sup>a</sup>  
(Thousands of Pounds, Crude Basis)

Fat or oil	Edible products	Soap	Paints, etc. <sup>b</sup>	Miscellaneous
Babassu oil.....	721	14,581	0	461
Castor oil.....	0	9,041	36,487	46,695
Coconut oil.....	122,870	511,313	509	95,763
Corn oil.....	67,238	446	8	4,401
Cottonseed oil.....	970,530	920	42	4,433
Fish and fish-liver oils.....	50	42,540	38,978	120,194
Marine-mammal oils	0	10	44	21,191
Lard.....	107,501	5,973	20	1,479
Linseed oil.....	0	276	454,297	49,792
Oiticica oil.....	0	0	9,600	2,032
Olive oil, edible.....	195	4	0	59
Olive oil, inedible and foots.....	0	764	0	36
Palm oil.....	0	1,091	5	41,799
Peanut oil.....	92,787	374	3	5,170
Rapeseed oil.....	—	0	3	11,549
Soybean oil.....	1,092,751	5,375	113,907	81,637
Tallow, edible and derived products.....	80,522	7,127	0	1,340
Tallow and greases, inedible <sup>c</sup> .....	0	1,526,192	355	372,799
Tung oil.....	0	0	75,619	12,740
Other vegetable oils.....	6,491	720	4,758	3,927
<i>Total</i> .....	2,541,656	2,126,747	734,635	877,497

<sup>a</sup> U.S. Dept. Agr., *Agricultural Statistics—1948*.

<sup>b</sup> Includes paints, varnishes, linoleum, oilcloth, and printing inks, but no other drying-oil products.

<sup>c</sup> Includes neatsfoot oil and wool grease.

TABLE XII. Wholesale Prices of Different Fats and Oils in the U.S., 1945–1949.

Fat or oil	Grade	Container	Place of sale	Wholesale price, av., ¢/lb.		
				1945 <sup>a</sup>	1947 <sup>a</sup>	Oct. 1949 <sup>b</sup>
Butter	92 score	—	Chicago	42.3	70.6	62.1
Castor oil	No. 3	Drums	N.Y.	13.0	29.1	17.0
Coconut oil (Manila)	Crude	Tanks	Pacific Coast	11.0	20.7	16.0
Cod-liver oil (Norway)	U.S.P. XIII	Barrels	N.Y.	32.9	39.5	21.5
Corn oil	Crude	Tank cars	Midwestern mills	12.8	25.7	11.5
Cottonseed oil	Crude	Tank cars	Southeastern mills	12.8	25.9	10.2
Grease	Inedible, A white	Tank cars	Chicago	8.8	18.9	5.5
Lard	Prime steam	Loose	Chicago	12.8	22.5	11.9
Linseed oil	Raw	Tank cars	Minneapolis	14.3	32.8	17.3
Olive oil (California)	Edible	Drums	N.Y.	60.7	73.6	41.3
Palm oil (Congo)	Crude	Bulk	N.Y.	11.4	—	14.4
Peanut oil	Crude	Tank cars	Mills	13.0	26.3	11.5
Rapeseed oil	Refined, denatured	Bulk	N.Y.	11.6	32.0	—
Sardine oil	Crude	Tank cars	Pacific Coast	8.9	22.2	6.1
Soybean oil	Crude	Tank cars	Midwestern mills	11.8	23.3	10.1
Tallow	Edible	Tank cars	Chicago	9.9	20.5	7.3
Tallow	Prime or extra	Tank cars	Chicago	8.6	19.2	5.9
Tung oil	—	Drums	N.Y.	39.0	30.5	27.2

<sup>a</sup> U.S. Dept. Agr., *Agricultural Statistics—1948*.

<sup>b</sup> U.S. Dept. Agr., Bur. Agr. Economics, *The Fats & Oils Situation*, November 1949.

Recent data on consumption and foreign trade in other countries are not generally available. In the past, all of the western European countries have been highly dependent upon Africa, South America, and the Orient for supplies of oils and fats and oil-bearing seeds.

The prices of fats and oils are characterized by greater variation than most commodities. Prices of selected fats and oils during the period 1945-1949 are given in Table XII.

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A. E. BAILEY

## FATTY ACIDS

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## SURVEY

The fatty acids are a large group of aliphatic monocarboxylic acids, many of which occur as glycerides (esters of glycerol (*q.v.*)) in natural fats and oils (see also *Acids, carboxylic*; *Fats and fatty oils*). Some of them also occur as other esters in waxes (*q.v.*) and essential oils (see *Oils, essential*), and as free acids in tall oil (*q.v.*). See also *Acetic acid*; *Butyric acid*; *Formic acid*; *Propionic acid*.

Although the term "fatty acids" has been restricted by some to the saturated acids of the acetic acid series,  $C_nH_{2n+1}COOH$ , both normal and branched-chain, it is now generally used to include also related unsaturated acids, certain substituted acids (hydroxy and keto), and even aliphatic acids containing alicyclic substituents, as the chaulmoogra-oil acids (see p. 295). See Tables I-IV. Certain other alicyclic acids (naphthenic acids—*q.v.*), which contain no aliphatic chain, have also sometimes been loosely termed fatty acids and their salts called soaps (see *Driers and metallic soaps*).

The naturally occurring fatty acids (also called "fat acids") with a few exceptions are higher straight-chain unsubstituted acids containing an even number of carbon atoms. Although only a few branched-chain, hydroxy, and keto acids have been detected in naturally occurring fatty substances in appreciable amounts, a considerable number of these and also of odd-numbered acids have been prepared synthetically.

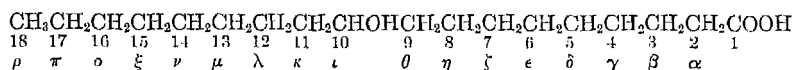
The unsaturated fatty acids can be divided, on the basis of the number of double bonds in the hydrocarbon chain, into *monoethenoid*, *diethenoid*, *triethenoid*, etc. (or *monoethylenic*, etc.). The *polyethenoid* acids may also be classified as nonconjugated or conjugated, depending upon the relative positions of the double bonds. If these bonds are separated by one or more single-bonded carbon atoms,  $-C=C-C_n-C=C-$   $C-$ , the acid is said to be *nonconjugated*. When double-bonded carbon atoms are adjacent to one another,  $-C=C-C=C-$ , the acid is referred to as *conjugated*. An

acid containing one or more triple-bonded carbon atoms is referred to as an *acetylenic* or *ethynoid* (*ethinoid*) acid.

## NOMENCLATURE

Of the three principal types of names for carboxylic acids (see Vol. I, p. 140), common names and I.U.P.A.C.-modified Geneva names are most used for fatty acids. Thus, palmitic acid,  $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ , so named from its occurrence in palm oil among other sources, is systematically called hexadecanoic acid from the corresponding hydrocarbon, hexadecane,  $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$ ; stearic acid,  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ , from Greek *stear*, tallow, is octadecanoic acid from octadecane,  $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_3$ . (Names like *n*-hexadecoic acid and *n*-hexadecylic acid are also still used to some extent.) Similarly, oleic acid,  $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$ , from Latin *oleum*, oil, is an octadecenoic acid; linoleic acid,  $\text{CH}_3(\text{CH}_2)_4\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$ , which occurs in linseed and other oils, is an octadecadienoic acid; and linolenic acid,  $\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$ , is an octadecatrienoic acid. Tauric acid,  $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{C}(\text{CH}_2)_4\text{COOH})_2$ , is an octadecynoic (octadecinoic) acid.

The positions in the higher fatty acids are usually designated for convenience by numbers instead of Greek letters, although  $\alpha$ -,  $\beta$ -, and  $\gamma$ - are frequently used and only Greek letters are employed with common names by *Chemical Abstracts*. For example:



Usual name: 10-Hydroxystearic acid

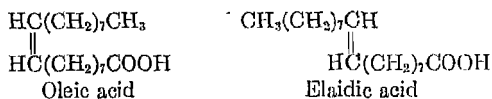
C.A. name: *l*-Hydroxystearic acid

I.U.P.A.C.-Geneva name: 10-Hydroxyoctadecanoic acid

However, the Greek letter  $\omega$  is often used to designate the terminal carbon atom (farthest from the carboxyl group) in any chain.

The positions of double and triple bonds in unsaturated acids are similarly indicated, the number indicating the lower-numbered of the two carbon atoms of the unsaturated linkage. Formerly (and still to some extent), the Greek letter  $\Delta$  was used to designate double and sometimes triple bonds, usually with two numbers to specify both attachments of each bond. Thus, oleic acid is 9-octadecenoic or  $\Delta^9$ -10-octadecenoic acid, linoleic acid is 9,12- or  $\Delta^{9,10,12,13}$ -octadecadienoic acid, and stearolic acid is 9- or  $\Delta^{9,10}$ -octadecynoic acid.

Since like other ethylenic compounds fatty acids containing one or more double bonds exhibit geometric isomerism (see *Stereochemistry*), the *cis* and *trans* forms are also indicated when known. With systematic names it is necessary to designate the isomers by the use of the prefixes *cis*- and *trans*-. However, in the case of naturally occurring acids and certain synthetic acids with a common name, this name alone is sufficient if it refers specifically to one form, usually the common natural or normal isomeric form; oleic acid, for example, is the *cis* form and elaidic acid the corresponding *trans* form:



In other common names containing -oleic and -laidic (or elaido-), the former usually denotes a *cis* form and the latter a *trans* form: myristoleic is thought to be *cis*-9-tetradecenoic and petroselaidic is *trans*-6-octadecenoic. Again, if two or more double bonds are present, the isomeric forms resulting from each such bond must be indicated in systematic names but not usually in common names. Thus, linoleic denotes specifically *cis*-9,*cis*-12-octadecadienoic, and linolelaidic, *trans*-9,*trans*-12-octadecadienoic.

Because of the large number of possible isomeric unsaturated acids (both positional and geometric isomers) and the difficulty of isolating and identifying them, there is still great confusion in the names of many of the acids in the literature. Common names have been extended to include other isomers: *trans*-oleic has been used as a synonym for elaidic, and linoleic sometimes denotes any unsaturated straight-chain fatty acid containing 18 carbon atoms and two double bonds. On the other hand, the prefix *iso*- has sometimes been used broadly to designate any isomers of well-known acids,

TABLE I. Saturated Fatty Acids.

Common name	Synonyms	Formula	Formula weight	M <sub>n</sub> , g./mole	B.p., °C.	d <sub>4</sub> <sup>20</sup>	n <sub>D</sub> <sup>20</sup>	Neutralization value
Formic	Methanoic	HC(=O)OH	46.03	8.4	100.5	1.220	1.3714	1218.96
Acetic	Ethanoic	CH <sub>3</sub> COOH	60.05	16.6	118.1	1.049	1.3718	934.26
Propionic	Propanoic	C <sub>2</sub> H <sub>5</sub> COOH	74.08	-22	141.1	0.992	1.3874	757.36
Butyric	Butanoic	C <sub>3</sub> H <sub>7</sub> COOH	88.10	-7.9	163.5	0.959	1.39906	636.79
Valeric	Pentanoic	C <sub>4</sub> H <sub>9</sub> COOH	102.13	-34.5	187.0	0.942	1.4086	549.34
Caproic	Hexanoic	C <sub>5</sub> H <sub>11</sub> COOH	116.15	-3.4	205.8	0.929	1.4170	483.00
Enanthic	Heptanoic	C <sub>6</sub> H <sub>13</sub> COOH	130.18	-10.5	223.0	0.922	1.4230	430.96
Caprylic	Octanoic	C <sub>7</sub> H <sub>15</sub> COOH	144.21	16.7	239.7	0.910	1.4280	389.05
Pelargonic	Nonanoic	C <sub>8</sub> H <sub>17</sub> COOH	158.23	12.5	255.6	0.907	1.4322	354.56
Capric	Decanoic	C <sub>9</sub> H <sub>19</sub> COOH	172.26	31.6	270.0	0.895 <sup>20</sup>	1.4169 <sup>20</sup>	325.69
<i>n</i> -Undecylic	Undecanoic; hendecanoic	C <sub>10</sub> H <sub>21</sub> COOH	186.29	29.3	284.0	0.9905 <sup>25</sup>	1.4202 <sup>20</sup>	301.17
Lauric	Dodecanoic	C <sub>11</sub> H <sub>23</sub> COOH	200.31	44.2	298.9	0.883	1.4230 <sup>20</sup>	280.08
<i>n</i> -Tridecyllic	Tridecanoic	C <sub>12</sub> H <sub>25</sub> COOH	214.34	41.5	312.4	0.8458 <sup>30</sup>	1.4252 <sup>20</sup>	261.75
Myristic	Tetradecanoic	C <sub>13</sub> H <sub>27</sub> COOH	228.36	53.9	326.2	0.838 <sup>60</sup>	1.4273 <sup>20</sup>	245.68
<i>n</i> -Pentadecylic	Pentadecanoic	C <sub>14</sub> H <sub>29</sub> COOH	242.39	52.3	339.1	0.8423 <sup>51</sup>	1.4292 <sup>20</sup>	231.46
Palmitic	Hexadecanoic	C <sub>15</sub> H <sub>31</sub> COOH	256.42	63.1	351.5	0.8334 <sup>52</sup>	1.4309 <sup>20</sup>	218.80
Margaric	Heptadecanoic	C <sub>16</sub> H <sub>33</sub> COOH	270.44	61.3	363.8	0.853 <sup>60</sup>	1.4324 <sup>20</sup>	207.45
Stearic	Octadecanoic	C <sub>17</sub> H <sub>35</sub> COOH	284.47	69.6	376.1	0.84769 <sup>3</sup>	1.4337 <sup>20</sup>	197.23
<i>n</i> -Nonadecylic	Nonadecanoic	C <sub>18</sub> H <sub>37</sub> COOH	298.49	68.6	299 <sup>100</sup>	0.8771 <sup>24</sup>	1.4512 <sup>25</sup>	187.96
Arachidic	Eicosanoic; arachic	C <sub>19</sub> H <sub>39</sub> COOH	312.52	75.3	203-205 <sub>1</sub>	0.8240 <sup>200</sup>	1.4250 <sup>100</sup>	179.52
<i>n</i> -Heneicosoic	Heneicosanoic	C <sub>20</sub> H <sub>41</sub> COOH	326.55	74.3	—	—	—	171.81
Behenic	Docosanoic	C <sub>21</sub> H <sub>43</sub> COOH	340.57	79.9	306 <sup>35</sup>	0.8221 <sup>102</sup>	1.4270 <sup>100</sup>	164.73
<i>n</i> -Tricosoic	Tricosanoic	C <sub>22</sub> H <sub>45</sub> COOH	354.60	79.1	—	—	—	158.22
Lignoceric	Tetracosanoic	C <sub>23</sub> H <sub>47</sub> COOH	368.62	84.2	—	0.8207 <sup>100</sup>	1.4287 <sup>100</sup>	152.20
<i>n</i> -Pentacosoic	Pentacosanoic	C <sub>24</sub> H <sub>49</sub> COOH	382.65	83.5	—	—	—	146.62
Cerotic	Hexacosanoic	C <sub>25</sub> H <sub>51</sub> COOH	396.68	87.7	dec.	0.8198 <sup>105</sup>	1.4301 <sup>122</sup>	141.44
<i>n</i> -Heptacosoic	Heptacosanoic	C <sub>26</sub> H <sub>53</sub> COOH	410.70	87.6	—	—	—	136.60
Montanic	Octacosanoic	C <sub>27</sub> H <sub>55</sub> COOH	424.73	90.0	—	0.8191 <sup>122</sup>	1.4313 <sup>100</sup>	132.09
<i>n</i> -Nonacosoic	Nonacosanoic	C <sub>28</sub> H <sub>57</sub> COOH	438.75	90.3	—	—	—	127.87
Melissic	Triacontanoic	C <sub>29</sub> H <sub>59</sub> COOH	452.78	93.6	—	—	1.4323 <sup>103</sup>	123.91
<i>n</i> -Hentriacontic	Hentriacontanoic	C <sub>30</sub> H <sub>61</sub> COOH	466.80	93.1	—	—	—	120.19
<i>n</i> -Dotriacontic	Dotriacontanoic	C <sub>31</sub> H <sub>63</sub> COOH	480.83	96.2	—	—	—	116.68
<i>n</i> -Tetraatriacontic	Tetraatriacontanoic	C <sub>32</sub> H <sub>65</sub> COOH	508.88	98.4	—	—	—	110.24
Ceroplactic	Pentatriacontanoic	C <sub>33</sub> H <sub>67</sub> COOH	522.91	98.3-98.5	—	—	—	107.28
<i>n</i> -Hexatriacontic	Hexatriacontanoic	C <sub>34</sub> H <sub>69</sub> COOH	536.94	99.9	—	—	—	104.49
<i>n</i> -Octatriacontic	Octatriacontanoic	C <sub>37</sub> H <sub>75</sub> COOH	564.99	101.6	—	—	—	99.30
<i>n</i> -Hexatetracontic	Hexatetracontanoic	C <sub>35</sub> H <sub>71</sub> COOH	677.20	106.8	—	—	—	82.85

<i>Branched-chain acids</i>								
$\alpha$ -Methylbutyric	2-Methylbutanoic; <i>dextro</i> -valeric	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COOH}$	102.13	< -80	176-177	0.9419	1.4051	549.34
Isovaleric	3-Methylbutanoic	$(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$	102.13	-37.6	176.7	0.937 <sup>16</sup>	1.40178 <sup>22,4</sup>	549.34
Pivalic	2,2-Dimethylpropanoic; trimethyl-acetic	$(\text{CH}_3)_3\text{CCOOH}$	102.13	35.5	163.8	0.905 <sup>49</sup>	1.3931 <sup>46,5</sup>	549.34
2-Ethylhexoic	2-Ethylhexanoic; octoic	$\text{CH}_3(\text{CH}_2)_8\text{CH}(\text{C}_2\text{H}_5)\text{COOH}$	144.21	-118.4	226.9	0.9077 <sup>20</sup>	1.4252	389.05

TABLE II. Monoethenoid Fatty Acids.

Common name	Synonyms	Formula	M.p., °C.	B.p., °C.	$d_4^{25}$	$n_D^{25}$	Neutralization value	Theoretical iodine value
Octuic	4-Deenoic	$\text{CH}_3(\text{CH}_2)_5\text{CH}:\text{CH}(\text{CH}_2)_2\text{COOH}$	—	148-150 <sub>13</sub>	0.9197	1.4497	329.55	149.10
Caproic	<i>cis</i> -9-Decenoic	$\text{CH}_2:\text{CH}(\text{CH}_2)_7\text{COOH}$	—	142	0.9238 <sup>15</sup>	1.4488	329.55	149.10
10-Undecylenic	10-Undecenoic; 10-Heu-decenoic	$\text{CH}_2:\text{CH}(\text{CH}_2)_8\text{COOH}$	24.5	275	0.9072 <sup>24</sup>	—	—	—
Lauroic	<i>cis</i> -9-Dodecenoic	$\text{CH}_3\text{CH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	—	—	0.9130 <sup>15</sup>	1.4335 <sup>15</sup>	282.93	128.01
Physeteric	5-Tetradecenoic	$\text{CH}_2(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_5\text{COOH}$	—	—	0.9046	1.4552	247.87	112.15
Myristoleic	<i>cis</i> -9-Tetradecenoic	$\text{CH}_3(\text{CH}_2)_3\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	—	—	0.9018	1.4549	247.87	112.15
Palmitoleic	<i>cis</i> -9-Hexadecenoic	$\text{CH}_3(\text{CH}_2)_5\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	-0.5 to 0.5	—	0.86369 <sup>70</sup>	1.44103 <sup>70</sup>	220.53	99.78
Petroselinic	<i>cis</i> -6-Octadecenoic	$\text{CH}_3(\text{CH}_2)_6\text{CH}:\text{CH}(\text{CH}_2)_8\text{COOH}$	30	—	0.8681 <sup>40</sup>	1.4533 <sup>40</sup>	198.63	89.87
Petroselinic	<i>trans</i> -6-Octadecenoic	$\text{CH}_3(\text{CH}_2)_6\text{CH}:\text{CH}(\text{CH}_2)_8\text{COOH}$	54	—	—	—	198.63	89.87
Oleic	<i>cis</i> -9-Octadecenoic	$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	13.4 ( $\alpha$ -)	234-235 <sub>15</sub>	0.8905	1.45823	198.63	89.87
			16.3 ( $\beta$ -)					
Elaidic	<i>trans</i> -9-Octadecenoic	$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	46.5	234 <sub>13</sub>	0.85682 <sup>90</sup>	1.44053 <sup>90</sup>	198.63	89.87
Vaccenic	<i>trans</i> -11-Octadecenoic	$\text{CH}_3(\text{CH}_2)_8\text{CH}:\text{CH}(\text{CH}_2)_5\text{COOH}$	42.5	—	0.8563 <sup>70</sup>	1.4406 <sup>70</sup>	198.63	89.87
Gadoleic	<i>cis</i> -9-Eicosenoic	$\text{CH}_3(\text{CH}_2)_9\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	—	—	—	—	180.89	81.75
Cetoleic	11-Docosenoic	$\text{CH}_3(\text{CH}_2)_9\text{CH}:\text{CH}(\text{CH}_2)_9\text{COOH}$	—	—	—	—	165.72	74.98
Erucic	<i>cis</i> -13-Docosenoic	$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_9\text{COOH}$	34.7	281 <sub>30</sub>	0.85321 <sup>70</sup>	1.44438 <sup>70</sup>	165.72	74.98
Brassicic	<i>trans</i> -13-Docosenoic	$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_9\text{COOH}$	61.9	265 <sub>13</sub>	0.85002 <sup>70</sup>	1.44349 <sup>70</sup>	165.72	74.98
Selacholeic	<i>cis</i> -15-Tetracosenoic; nervonic	$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_{15}\text{COOH}$	42.5	—	—	—	153.04	69.24
Ximenic	17-Hexacosenoic	$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_{18}\text{COOH}$	—	—	—	—	142.16	64.32
Lumequeic	21-Triacontenoic	$\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_{25}\text{COOH}$	—	—	—	—	124.46	56.31

TABLE III. Di-, Tri-, and Other Polyethenoid Fatty Acids.

Common name	Synonyms	Formula	M.p., °C.	B.p., °C.	$d_4^{20}$	$n_D^{20}$	Neutralization value	Theoret. iodine value
Sorbic	2,4-Hexadienoic	$\text{CH}_3\text{CH}:\text{CHCH}:\text{CHCOOH}$	134.5	228 (dec.)	—	—	500.37	226.39
Linoleic	<i>cis</i> -9, <i>cis</i> -12-Octadecadienoic; linolic	$\text{CH}_3(\text{CH}_2)_4\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	-5.0 to -5.27	202 <sub>1,4</sub>	0.9038 <sup>18</sup>	1.4699	200.06	181.03
Linolelaidic	<i>trans</i> -9, <i>trans</i> -12-Octadecadienoic	$\text{CH}_3(\text{CH}_2)_4\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	28-29	—	—	—	200.06	181.03
Hiragonic	6,10,14-Hexadecatrenoic	$\text{CH}_3\text{CH}:\text{CH}(\text{CH}_2)_3\text{CH}:\text{CH}(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_4\text{COOH}$	—	—	0.9288	1.4855	224.08	304.16
$\alpha$ -Eleostearic	<i>cis</i> -9, <i>cis</i> -11, <i>trans</i> -13-Octadecatrenoic (?)	$\text{CH}_3(\text{CH}_2)_3\text{CH}:\text{CHCH}:\text{CHCH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	48-49	235 <sub>12</sub>	0.9028 <sup>20</sup>	1.5112 <sup>20</sup>	201.51	273.51
$\beta$ -Eleostearic	<i>trans</i> -9, <i>cis</i> -11, <i>cis</i> -13-Octadecatrenoic (?)	$\text{CH}_3(\text{CH}_2)_3\text{CH}:\text{CHCH}:\text{CHCH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	71.5	—	0.8909 <sup>15</sup>	1.5022 <sup>15</sup>	201.51	273.51
Punicic	9,11,13-Octadecatrenoic	$\text{CH}_3(\text{CH}_2)_3\text{CH}:\text{CHCH}:\text{CHCH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	43.5-44	—	—	—	201.51	273.51
Linolenic	<i>cis</i> -9, <i>cis</i> -12, <i>cis</i> -15-Octadecatrenoic	$\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	-11.0 to -11.3	157-158 <sub>1,001</sub>	0.9046	1.4780	201.51	273.51
Elaidolinolenic	<i>trans</i> -9, <i>trans</i> -12, <i>trans</i> -15-Octadecatrenoic (?)	$\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	29-30	—	—	—	201.51	273.51
Pseudoeleostearic	<i>trans</i> -10, <i>trans</i> -12, <i>trans</i> -14-Octadecatrenoic	$\text{CH}_3(\text{CH}_2)_2\text{CH}:\text{CHCH}:\text{CHCH}:\text{CH}(\text{CH}_2)_8\text{COOH}$	79	—	—	—	201.51	273.51
Morostic	4,8,12,15-Octadecatetraenoic	$\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_2\text{CH}:\text{CH}(\text{CH}_2)_3\text{COOH}$	—	—	0.9297	1.4911	202.98	367.31
$\alpha$ -Parinaric	9,11,13,15-Octadecatetraenoic	$\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}:\text{CHCH}:\text{CH}(\text{CH}_2)_3\text{COOH}$	85-86	—	—	—	202.98	367.31
$\beta$ -Parinaric	9,11,13,15-Octadecatetraenoic	$\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}:\text{CHCH}:\text{CH}(\text{CH}_2)_3\text{COOH}$	95-96	—	—	—	202.98	367.31
Arachidonic	5,8,11,14-Eicosatetraenoic	$\text{CH}_3(\text{CH}_2)_4\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_3\text{COOH}$	-49.5	—	—	1.4824	184.28	333.50
Clupanodonic	4(?),8,12,15,19-Docosapentaenoic	$\text{CH}_3\text{CH}_2\text{CH}:\text{CH}(\text{CH}_2)_3\text{CH}:\text{CH}(\text{CH}_2)_2\text{CH}:\text{CH}(\text{CH}_2)_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	—	—	0.9356	1.5020	169.76	384.03
Nistic	4(?),8,12,15,18,21-Tetracosahexaenoic	$\text{CH}_3\text{CH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_2\text{CH}:\text{CH}(\text{CH}_2)_3\text{COOH}$	—	—	—	—	157.36	427.19

TABLE IV. Ethynoid and Substituted Ethenoid Fatty Acids.

Common name	Synonyms	Formula	M.p., °C.	B.p., °C.	$d_4^{20}$	$n_D^{20}$	Neutralization value	Theoret. iodine value
<i>Ethynoid acids</i>								
Propiolic	2-Propynoic; propargylic	HC:CCOOH	9	144	1.139 <sup>15</sup> <sub>15</sub>	1.43146 <sup>15</sup>	800.96	724.78
Tetrollic	2-Butynoic	CH <sub>3</sub> C:CCOOH	76	203	—	—	667.33	603.86
4-Pentynoic	—	HC:C(CH <sub>2</sub> ) <sub>2</sub> COOH	57	203-204 <sup>608</sup>	—	—	571.92	517.51
Dehydroun-decylenic	10-Undecynoic	HC:C(CH <sub>2</sub> ) <sub>8</sub> COOH	43	175 <sub>15</sub>	—	—	307.83	278.55
Tariric	6-Octadecynoic	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> C:C(CH <sub>2</sub> ) <sub>4</sub> COOH	51.5	—	—	—	200.06	181.03
Stearolic	9-Octadecynoic	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> C:C(CH <sub>2</sub> ) <sub>7</sub> COOH	48	260	—	—	200.06	181.03
Behenolic	13-Docosynoic	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> C:C(CH <sub>2</sub> ) <sub>11</sub> COOH	57	—	—	—	166.71	150.85
Isamic	Octadec-17-enedi-9,11(?)ynoic; erythrogonic	CH <sub>3</sub> :CH(CH <sub>2</sub> ) <sub>4</sub> C:CC:C(CH <sub>2</sub> ) <sub>7</sub> COOH	39.5	—	0.9309 <sup>15</sup>	1.49148 <sup>60</sup>	204.47	462.55
<i>Substituted acids</i>								
Ricinoleic	12-Hydroxy-cis-9-octadecenoic; ricinolic	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CHOHCH <sub>2</sub> CH:CH(CH <sub>2</sub> ) <sub>7</sub> COOH	4-5	—	0.940 <sup>17,2</sup> <sub>15,3</sub>	1.4716	187.98	85.05
Licanic	4-Oxo-9,11,13-octadecatrienoic; conepic	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH:CHCH:CHCH:CH(CH <sub>2</sub> ) <sub>2</sub> COOH	74-75 (α-) 99.5 (β-)	—	—	—	191.87	260.43



as isooleic acids (see p. 163). Greek letters have also been employed in an attempt to distinguish between isomers, as  $\alpha$ - and  $\beta$ -eleostearic acids.

Optical isomerism, resulting from the presence of one or more asymmetric carbon atoms, occurs only in branched-chain and substituted fatty acids, as ricinoleic acid (see p. 290) and chaulmoogra-oil acids (see p. 295). Various systems of naming the stereoisomers have been used, including (+)- and (-)- to indicate direction of rotation, and carbohydrate prefixes such as *D-threo*- and *L-erythro*- and *D-ribo*- and *L-xylo*- (see Vol. 2, p. 871; *Stereochemistry*), as in dihydroxystearic acid (see p. 219). The prefixes *cis*- and *trans*- have also often been used erroneously to denote such configurations.

The conventional way to name acyl radicals has been to change the ending "-ic acid" to "-yl," as in formyl from formic acid. Geneva names involve this same change of -ic to -yl (or -oic to -oyl): heptanoyl from heptanoic. The unfortunate use of the same name for related alkyl and acyl radicals in a few instances has caused ambiguity. Lauryl, for example, may mean  $C_{12}H_{25}-$  or  $C_{11}H_{23}CO-$ . Palmityl and stearyl are similar offenders. To meet this situation, Geneva names are recommended for these alkyl radicals: dodecyl, hexadecyl, and octadecyl. Also adoption of -oyl rather than -yl has been commonly practiced for these acyl radicals: lauroyl, palmitoyl, and stearyl. In September 1949, the I.U.P.A.C. Commission on Organic Nomenclature made a recommendation that the -oyl ending be used for all fatty acyl radicals except formyl and acetyl. Thus, approved synonyms for butyryl and valeryl are butyroyl and valeroyl (see Table XX, p. 219).

**Saturated Acids ( $C_nH_{2n+1}COOH$ ).** The series of known saturated straight-chain acids from formic ( $C_1$ ) to octatriacontanoic ( $C_{38}$ ) is complete except for two or three odd-numbered acids above  $C_{31}$ . All of the even-numbered acids occur either in the free or combined state in nature, and all of them from butyric to octatriacontanoic are present either as glycerides or as monoesters in fats or waxes. Palmitic acid,  $C_{16}H_{34}O_2$ , is the most abundant saturated acid, and is present in practically all plant and animal fats. Stearic acid,  $C_{18}H_{36}O_2$ , is less abundant, but has a wide distribution. Its ease of preparation makes it the best-known and most important higher saturated acid.

Although various odd-numbered acids have been reported to occur naturally, they are probably mixtures of even-numbered acids. The only natural odd-carbon acids known with certainty are formic acid and isovaleric acid, but the remainder have been synthesized.

The naturally occurring saturated fatty acids, with some exceptions, do not exhibit any isomerism. However, branched-chain isomers of the straight-chain acids occur in bacteria (tuberculoic acid), in wool fat (two series of methyl-substituted acids), and in some marine animals and in valerian root (isovaleric acid) (see pp. 262, 284). Many other branched-chain acids have been synthesized in recent years. Substituted saturated fatty acids exhibit positional isomerism. This is observed in only a few natural acids but it occurs in many synthetic acids, for example, hydroxy and keto acids, which have been prepared in considerable number.

The lower members of the saturated fatty acid series are liquids at ordinary temperatures, but as the series is ascended the individual members become increasingly more viscous and ultimately pass to crystalline solids.

**Unsaturated Acids.** Both mono- and polyethenoid acids are widely distributed in plant, marine-, and land-animal oils. Land-animal fats usually contain smaller amounts of polyethenoid acids than do plant and marine oils, whereas marine oils are characterized by highly unsaturated acids (see p. 285).

The most abundant of all the naturally occurring fatty acids, saturated as well as unsaturated, is oleic acid (*cis*-9-octadecenoic acid). Unsaturated vegetable oils predominate in  $C_{16}$  and  $C_{18}$  acids, whereas in marine-animal oils the acids range from  $C_{16}$  to  $C_{26}$  with  $C_{20}$  and  $C_{22}$  predominating. In vegetable oils, the first double bond is usually at the 9,10-position, as in oleic acid, whereas in marine-oil acids it is often in the 4,5-position.

Unsaturated acids in general show three types of isomerism: chain or group isomerism, positional isomerism, and (in the case of ethylenic acids) geometric or *cis-trans* isomerism. Chain isomerism occurs in a number of cases, for example, linoleic and chaulmoogric acids,  $C_{15}H_{32}O_2$ ; linolenic and goric acids,  $C_{18}H_{30}O_2$ .

In many more cases there is variation only in the position of the double or triple bond or bonds in a chain. Octadecenoic acid,  $C_{18}H_{34}O_2$ , occurs naturally in at least three positionally isomeric forms, namely oleic or *cis*-9-octadecenoic acid, petroselinic or *cis*-6-octadecenoic, and vaccenic or *trans*-11-octadecenoic acid, and other isomers have been synthesized. The melting points of the natural and synthetic octadecenoic acids from 2- to 12- have been tabulated (see p. 48 of ref. 6). When two or more double bonds are present, the number of possible positional isomers is, of course, increased. However, only a few such isomers have been detected with certainty in natural fats, and most of these belong to the trienoic acid series.

*Cis-trans* isomers, in general, exhibit regular differences in physical properties. The *cis* form usually has the lower melting point (see p. 57 of ref. 6), the greater solubility in inert solvents, the higher heat of combustion, and, in the case of acids, the higher ionization constant. The unsymmetrical *cis* form exhibits a considerably higher dipole moment than the more symmetrical *trans* form. The x-ray spacing of the *cis* form is shorter than that of the *trans* form. The *cis* form is almost always the one found in nature, whereas the *trans* form is generally produced by treatment of the *cis* form by chemical and physical agents. Occasionally, *trans* acids are found in nature, for example, vaccenic acid, which is present in milk fat, tallow, etc. In most cases the *cis* form is labile and the *trans* form stable, but, if the two forms are of the same approximate stability, equilibrium inversion will occur by proper treatment of either form. For the oleic-elaidic transformation, equilibrium is attained at 66% of elaidic acid.

Any of the naturally occurring *cis* acids can be converted into the *trans* form by treatment with appropriate reagents such as the oxides of nitrogen, sulfur, and selenium. The inversion of a *cis* acid to a *trans* acid is frequently called elaidinization.

Since the number of geometric isomers increases exponentially with the number of double bonds, acids with two nonadjacent, nonterminal double bonds can exist in  $2^2$  or 4 forms, triethenoid in  $2^3$  or 8 forms, etc. All of the possible isomers are not known with certainty, even in the case of the four geometric isomers of linoleic acid, but many studies have been made of the optically isomeric bromination and oxidation products of linoleic and linolenic acids (see p. 55 of ref. 6; pp. 121, 132 of ref. 7). (See also *Stereochemistry*.)

*Monoethenoid Acids* ( $C_nH_{2n-1}COOH$ ). The naturally occurring monoethenoid acids generally have a chain length above  $C_9$ . Of the vegetable-oil unsaturated acids, the next most important to oleic,  $C_{18}H_{34}O_2$ , is palmitoleic,  $C_{16}H_{30}O_2$ , another 9,10-monoethylenic acid (9-hexadecenoic). Both are widely distributed in nature and, in frequency of occurrence, constitute the predominant natural acids of the monoethenoid series, just as palmitic and stearic acids constitute the predominant natural acids of the saturated series. The principal vegetable-oil unsaturated acids with no double bonds in the 9,10-position are petroselinic,  $C_{18}H_{34}O_2$ , and erucic,  $C_{22}H_{42}O_2$ . These acids, which have double bonds in the 6,7- and 13,14-positions, respectively, comprise 70-80% of the total fatty acids of a few seed fats. In addition to the monoethenoid acids isolated from natural sources, many have been prepared synthetically, including both odd and even members of the series, with the double bonds in various positions.

*Polyethenoid Acids.* Both conjugated and nonconjugated acids occur in vegetable oils, but practically no conjugated acids occur in marine-animal oils. Only two of the polyethenoid acids, namely, linoleic and linolenic acids, containing two and three double bonds, respectively, can be considered to occur in nature with appreciable frequency. No ayclic polyethenoid fatty acids containing less than 18 carbon atoms (with the exception of sorbic acid,  $\text{CH}_3\text{CH}:\text{CHCH}:\text{CHCOOH}$ ) are known with certainty to occur in plant fats.

Although the introduction of two or more double bonds in the carbon chain provides increased opportunity for the formation of positional as well as geometric isomers, actually fewer isomeric polyethenoid than monoethenoid acids have as yet been detected in natural fats. For example, the only isomeric diethenoid fatty acids known to occur naturally are ordinary linoleic acid and an isomer in some fish oils, where several groups of two and three isomeric monoethenoid acids have been identified from natural sources.

The triethenoid series, on the other hand, is represented by the well-known linolenic acid and several isomers, both positional and geometric. The trienoid acids, almost without exception, contain  $\text{C}_{18}$  carbon chains and the three double bonds are either in isolated or in conjugated positions. One  $\text{C}_{16}$  acid, hiragonic (6,10,14-hexadecatrienoid), has been reported as a minor component of Japanese sardine oil. Eicosatetraenoic acid (9,11,13-octadecatrienoid acid) occurs in tung and several related oils, and another 9,11,13-isomer (geometric) has been reported, namely, puniceic acid from pomegranate oil.

The tetraethenoid acid series is represented by the conjugated acid parinaric (probably 9,11,13,15-octadecatetraenoic) and the nonconjugated arachidonic acid (5,8,11,14-eicosatetraenoic acid), and by others in marine oils. Parinaric acid is the only one containing four double bonds that has thus far been isolated from seed fats. The naturally occurring modification, or  $\alpha$ -form, melting at  $85\text{--}86^\circ\text{C}$ ., is readily converted to another modification, or  $\beta$ -form, melting at  $95\text{--}96^\circ\text{C}$ .

A number of other polyethenoid acids, primarily, if not entirely, of marine-animal origin, are known. They contain twenty or more carbon atoms and five to seven double bonds. Those of most frequent occurrence and in largest proportion contain  $\text{C}_{20}$  and  $\text{C}_{22}$  skeletons. Considerable uncertainty exists with respect to the number and location of the double bonds in these acids (see "Marine-oil acids"). Clupanodonic (probably 4,8,12,15,19-docosapentaenoic acid,  $\text{C}_{22}\text{H}_{34}\text{O}_2$ ) occurs in practically all marine-animal oils.

*Ethynoid Acids.* Although many aliphatic triply bonded or ethynoid acids are known, only three have been identified with certainty as components of natural fats. Most of the many acids of this series prepared in the laboratory have a triple bond at either the  $\alpha$ - or  $\omega$ -position in the hydrocarbon chain, but stearolic acid (9-octadecynoic acid), the most studied of the acetylenic acids, corresponds to double-bonded oleic acid. Studies have been made of the fungicidal action of some triply bonded acids, particularly 9-undecynoic acid.

Of the three known naturally occurring ethynoid acids, tariric (6-octadecynoic) acid constitutes 90% of the glycerides of the seed fat of *Picramnia sora* found in Guatemala. It occurs also in relatively small amounts in other *Picramnia* species. An octadecenynoic acid has been isolated from the seeds of *Ongokea klaineana*; the unsaturated bonds are in the 6,7- and 9,10-positions, but the respective positions of

the double and triple bonds are unknown. Isamic acid, an octadecenediynoic acid, has also been isolated from seed oils of *Ongokea* species.

**Substituted Acids.** Substituting groups may be hydroxyl, keto, or cyclopentene rings. Many hydroxy acids occur naturally in wool fat (*q.v.*), brain lipides, bacteria, and in other animal fats. See "Hydroxy and keto acids"; "Chaulmoogra-oil acids."

### Physical Properties

Some of the most frequently used constants for the important fatty acids are given in Tables I-IV. Melting points and "long-spacing curves" are shown in Figure 17, page 204.

The properties of the fatty acids and their derivatives can be broadly divided into three groups: (1) properties characteristic of the liquid state; (2) properties characteristic of, or dependent upon, the crystal structure of the molecule; and (3) properties dependent upon the electronic, vibrational, or rotational energy of the molecule as evidenced by its spectral behavior.

#### VAPOR PRESSURE AND RELATED PROPERTIES

The vapor pressures, boiling points, heats of vaporization, and related properties have been measured for the first five members of the saturated fatty acid series with a relatively high degree of accuracy and have been known for a considerable time. Similar measurements for the  $C_6$ - $C_{18}$  acids have been made more recently.

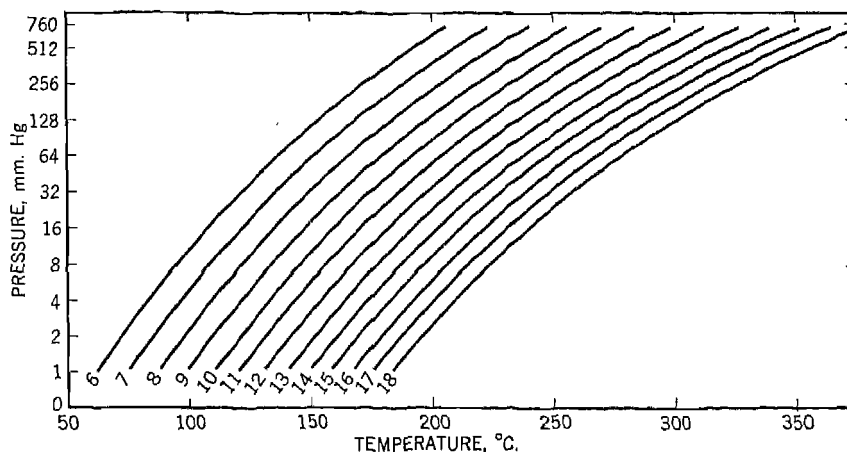


Fig. 1. Vapor pressures of saturated fatty acids from caproic to stearic (29).

The boiling temperatures at pressures ranging from 1 to 760 mm. Hg for the saturated acids from caproic to stearic are given by Pool and Ralston (29), who used these data to compute the values required to construct the corresponding vapor pressure-temperature curves (see Fig. 1). The pressure-temperature relations of the homologous series of acids from acetic to docosanoic for vacuum-steam distillation conditions over the pressure range 2 to 100 mm. Hg are given in Figure 2. While the latter values are not as accurate as those of Pool and Ralston for dry distillation, they are useful for practical vacuum-steam distillation operations and where more precise data

are lacking they may be considered to approximate the values that would be obtained by dry distillation.

Cramer determined the vapor pressures of the even-numbered fatty acids from caproic to stearic by a static method (10). Plotted as the logarithms of the pressure

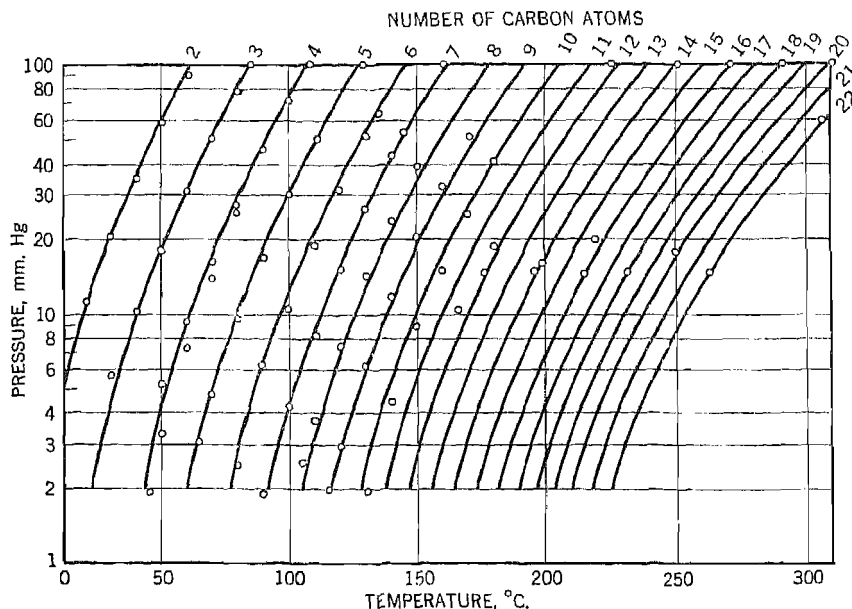


Fig. 2. Boiling points of the saturated fatty acids under conditions of vacuum-steam distillation (14).

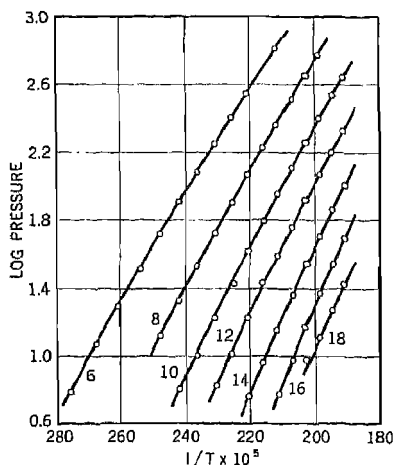


Fig. 3. Relationship between vapor pressure and temperature of even-numbered saturated fatty acids from caproic to stearic (10).

against the reciprocals of the corresponding temperature (see Fig. 3), the results lend themselves readily to the calculation of the corresponding heats of vaporization by means of the equation:

$$\frac{d \ln p}{d(1/T)} = - \frac{W}{R}$$

where  $W$  is the heat of vaporization per gram-mole,  $T$  the absolute temperature, and  $R$  the gas constant. The heats of vaporization calculated in this manner are given by Cramer (10). If desired, the heats of vaporization can be calculated from the data of Pool and Ralston (29) by use, in small pressure and temperature intervals, of the integrated form of the approximate Clausius-Clapeyron equation:

$$L = 4.576 \frac{T_2 T_1}{T_2 - T_1} \log \frac{p_2}{p_1}$$

where  $L$  is the heat of vaporization,  $p_1$  and  $p_2$  are pressures, and  $T_1$  and  $T_2$  are temperatures,

The boiling points of the saturated fatty acids increase with the number of carbon atoms, but the increase per carbon atom becomes less as the series is ascended. The higher members tend to undergo some decomposition even below atmospheric pressure. Association occurs in the vapor phase and the heat of association decreases with increase in the length of the carbon chain.

Distillations of acids are carried out commercially on a large scale for the purpose of separating mixtures of fatty acids. The boiling points (usually at atmospheric pressure) of a considerable number of alkyl esters of fatty acids will be found under *Esters, organic*. The boiling points at reduced pressure of the methyl esters of the even-numbered saturated acids from caproic to stearic have been given by Althouse and Triebold (8), together with decomposition pressures and temperatures. The corresponding vapor pressure-temperature curves extrapolated to 760 mm. Hg are shown in Figure 4. These data would be applicable in separating by distillation one saturated acid from another in a mixture of saturated acids. The boiling points over the range of 1 to 20 mm. Hg and the pressure-temperature relationships observed by Norris and Terry (27) for the methyl esters of myristic, palmitic, stearic, oleic, and linoleic acids are given in Figure 5. These data would be applicable in separating saturated from unsaturated

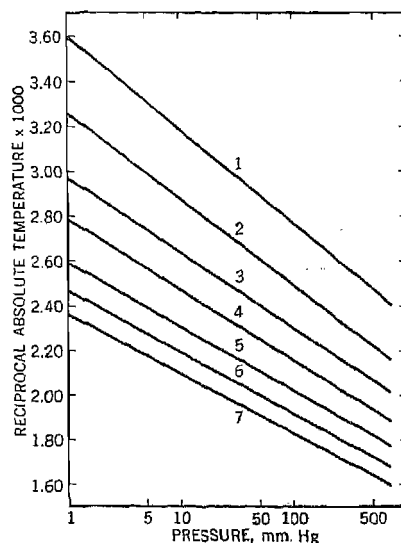


Fig. 4. Vapor pressures of methyl esters of even-numbered saturated fatty acids from caproic to stearic (p. 170 of ref. 6): 1, caproate; 2, caprylate; 3, caprate; 4, laurate; 5, myristate; 6, palmitate; and 7, stearate.

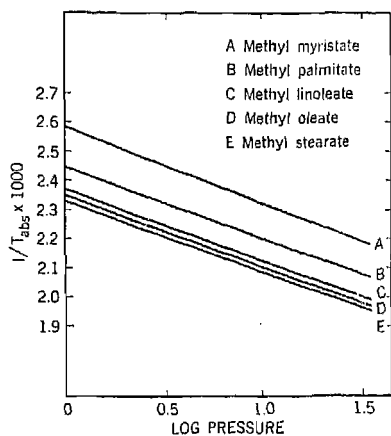


Fig. 5. Vapor pressures of methyl esters of some fatty acids (27).

acids by distillation. The calculated heats of vaporization have been determined by these authors.

Owing to the thermal instability of the long-chain unsaturated fatty acids and esters, accurate determinations of their boiling points are extremely difficult. These difficulties are reflected in the fragmentary, and, in part, conflicting data available.

#### REFRACTIVE INDEX

The refractive index is among the most useful characteristics of fatty acids and esters. Although numerous isolated measurements have been made of the refractive indexes of various fatty acids and esters, only a few systematic investigations have been made of this property and these are of relatively recent origin. In 1942, Dorinson, *et al.*, reported the refractive indexes of the saturated fatty acids from caproic to stearic, over a temperature range of 20 to 80°C. for the lowest-molecular acids and from just above

the melting point to 80°C. for the remainder of the series (11). The values for the refractive index in Figure 6 were corrected for effect of temperature by applying the factor  $0.00006(t - 20)$ , where  $t$  is the temperature at which the measurement was made. The refractivities for each acid fall on a straight line between 40 and 80°C. but, as indicated by the dotted line, deviate from linearity below 40°C.

No comparable data are available for the refractive indexes of the esters of the saturated fatty acids, but some individual values at a single temperature are given under *Esters, organic*. Mattil and Longenecker determined the variation in refractive index as a function of temperature for the series of methyl esters from caprate to stearate (25). They also determined the variation in refractive index as a function of

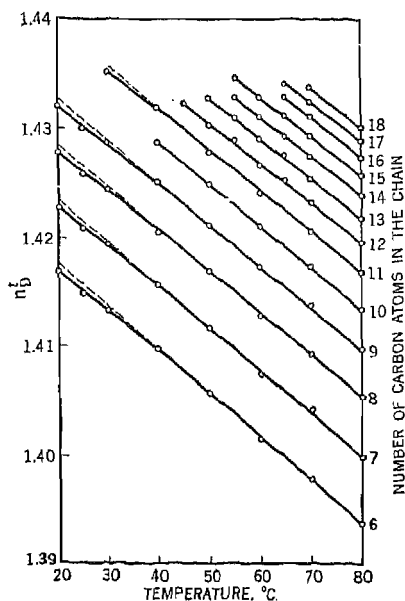


Fig. 6. Variation of refractive index with temperature of saturated fatty acids from caproic to stearic (11).

(see Fig. 7). Other curves relating the logarithms of the viscosities with the molecular weights of the normal fatty acids and their methyl and ethyl esters are approximately linear except for the first two acids (formic and acetic) of the series. The increment of decrease in the viscosity of the normal acids and esters with increasing temperature becomes continuously smaller.

Except for the methyl and ethyl esters of formic, acetic, and propionic acids, most of the values reported for the viscosities of esters refer to a single temperature (see p. 227 of ref. 6). In the unsaturated series, oleic and elaidic acids and their esters are the only higher ones that have received any appreciable attention (see Table V). The fluidities of the lower esters of oleic acid have been reported to be about four times as great as that of the acid, a fact that has been attributed to the very high molecular association of the acid. The fluidities of the esters increase about threefold over the temperature range 30 to 90°C., compared to a fivefold increase for the acid.

composition of a series of binary mixtures of the methyl esters of both saturated and unsaturated acids. The latter relationships are especially useful in following the fractionation of fatty acid mixtures by distillation or low-temperature crystallization. Few data are available on the refractive indexes of highly pure unsaturated acids and esters. Values for the refractive indexes of ethyl linoleate and ethyl linolenate calculated from butyrorrefractometer readings at various temperatures up to 60°C. are given by McCutcheon (24).

#### VISCOSITY

Owing to the differences in solidification points, it is not possible to compare the viscosities of an extended series of fatty acids at temperatures below 70°C. Data for the first four members of the saturated-acid series were tabulated by Thorpe and Rodger (see p. 224 of ref. 6). For the C<sub>5</sub>-C<sub>9</sub> acids and the even-numbered C<sub>12</sub>-C<sub>18</sub> acids, viscosity data are given in the form of temperature-viscosity curves

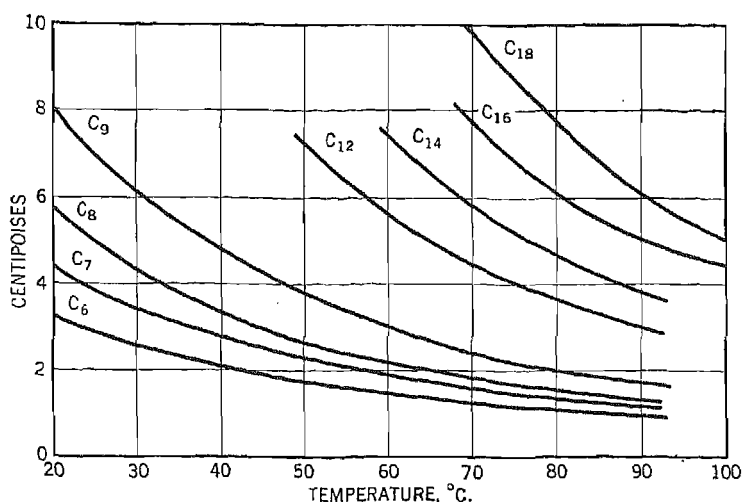


Fig. 7. Temperature-viscosity relationships of saturated fatty acids from caproic to stearic (p. 226 of ref. 6).

TABLE V. Viscosities of Oleic Acid and Its Esters.

Temp., °C.	Oleic acid		Methyl oleate		Ethyl oleate	
	$d_4^t$	$\eta$ , poises	$d_4^t$	$\eta$ , poises	$d_4^t$	$\eta$ , poises
20	0.8905	0.3880	—	—	—	—
25	0.8870	0.2764	—	—	—	—
30	0.8836	0.2301	0.8666	0.0488	0.8622	0.0518
35	0.8802 <sup>a</sup>	0.1946	—	—	—	—
45	0.8735 <sup>a</sup>	0.1408	—	—	—	—
60	0.8634	0.0941	0.8450 <sup>a</sup>	0.0262	0.8400	0.0276
90	0.8429	0.0485	0.8234 <sup>a</sup>	0.0164	0.8192	0.0171

<sup>a</sup> Interpolated.

Source: reference (20).

#### DENSITY AND RELATED PROPERTIES

**Density.** Although various isolated values for the densities and specific gravities of a considerable number of the fatty acids and esters are to be found in the literature, they are often not comparable because of the different temperatures employed in determining them. Data for the densities (in grams per milliliter) at different temperatures and, in some instances, for the specific volumes and temperature coefficients of the saturated fatty acids from  $C_6$  to  $C_{18}$  have been given by Garner and Ryder (13) and by Dorinson, *et al.* (11), and for the specific gravities or densities of some unsaturated acids and esters by Keffler and McLean (20).

The densities of the normal fatty acids in the liquid state are essentially a linear function of the temperature. In the liquid state at any given temperature, the density of the saturated fatty acids decreases with increase in molecular weight.

**Molar volumes** of various fatty acids and esters according to the calculations of Pauly (28), Garner and Ryder (13), Dorinson, *et al.* (11), and Keffler and McLean (20) are tabulated on pp. 214-17 of reference (6).

**Dilation.** The dilatometer permits continuous observation or measurement of the



change in volume of a substance in both the solid and liquid states, and, in addition, reveals other useful information such as changes from one polymorphic form to another and from solid to liquid (26,34). The melting point can be very accurately determined by use of the dilatometer and in the case of fats is one of the very few methods by which this can be done with a high degree of accuracy. Various types of dilatometers and the methods of applying them in investigations of fatty acids and natural fats have been described, but the modification devised by Bailey and Kraemer yields the most accurate and precise measurements (9).

### SOLUBILITY

**Miscible Aqueous Systems.** The normal fatty acids exhibit higher solubilities in water than do the corresponding hydrocarbons because of the polar or hydrophilic

TABLE VI. Solubilities of Saturated Fatty Acids in Water.

Acid	Soly., grams/100 grams water, at:		Acid	Soly., grams/100 grams water, at:	
	20°C.	60°C.		20°C.	60°C.
Formic.....	∞	∞	Capric.....	0.015	0.027
Acetic.....	∞	∞	Undecylic.....	0.0093	0.015
Propionic....	∞	∞	Lauric.....	0.0055	0.0087
Butyric.....	∞	∞	Tridecanoic.....	0.0033	0.0054
Valeric.....	3.7	—	Myristic.....	0.0020	0.0034
Caproic.....	0.968	1.171	Pentadecanoic....	0.0012	0.0020
Enanthic.....	0.244	0.353	Palmitic.....	0.00072	0.0012
Caprylic.....	0.068	0.113	Margaric.....	0.00042	0.00081
Pelargonic....	0.026	0.051	Stearic.....	0.00029	0.00050

Source: reference (30).

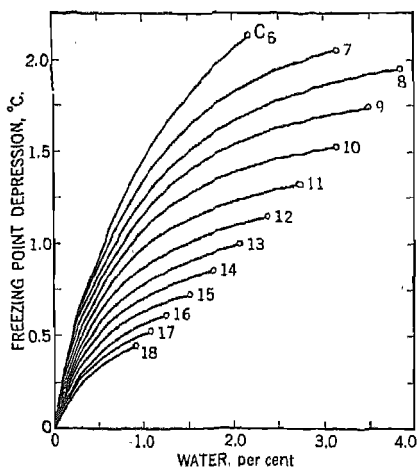


Fig. 8. Effect of addition of water on the freezing point of saturated fatty acids from caproic to stearic (15).

carboxyl group in the acids. The first four members of the saturated fatty acid series are miscible with water in all proportions at room temperature, but, as the hydrocarbon chain increases, the ability of the carboxyl group to bring about solubility of the acid in water becomes decreasingly effective and eventually acts merely to orient the fatty acid with respect to a water surface (see Table VI).

Eggenberger and co-workers (11a) reinvestigated the solubilities of some of the saturated acids in water and found them to be less soluble than indicated by the values in Table VI. For example, at 60°C., solubilities in gram/100 ml. solution were reported to be: caprylic, 0.1071; pelargonic, 0.0299; capric, 0.0100; undecylic, 0.0032; lauric, 0.00116; and myristic, 0.00056.

Hoerr, Pool, and Ralston determined the effect of the addition of water on the depression of the freezing point of the same series of fatty acids (see Fig. 8). These authors also determined the approximate solubilities of water in fatty acids (see Table VII). It may be seen that increasing the temperature increases the solubility of water

in low-molecular acids, but in the case of the higher members it has only a very small effect.

TABLE VII. Solubilities of Water in Saturated Fatty Acids.

Acid	Temp., °C.	Water, %	Acid	Temp., °C.	Water, %
Caproic.....	-5.4	2.21	Lauric.....	42.7	2.35
	12.3	4.73		75.0	2.70
	31.7	7.57		90.5	2.85
	46.3	9.70	Tridecanoic.....	40.8	2.00
Enanthic.....	-8.3	2.98	Myristic.....	53.2	1.70
	42.5	9.98	Pentadecanoic.....	51.8	1.46
Caprylic.....	14.4	3.88		90.0	1.62
Pelargonic.....	10.5	3.45	Palmitic.....	61.8	1.25
Capric.....	29.4	3.12	Margaric.....	60.4	1.06
Undecylic.....	26.8	2.72	Stearic.....	68.7	0.92
	57.5	4.21		92.4	1.02

Source: reference (15).

**Immiscible Aqueous Systems.** Although increasing the length of the hydrocarbon chain ultimately diminishes to the vanishing point the effect of the carboxyl group to induce solubility in water, the carboxyl group is still effective at a water-acid interface with respect to orientation of mono- and polymolecular films. Nonpolar liquids, such as the hydrocarbons, do not spread on water, but if the molecules contain a polar or hydrophilic group and a nonpolar or hydrophobic group, the liquid will spread. Furthermore, most of the films formed in this manner are only one molecule thick and for any given substance have all their molecules similarly oriented, often simply perpendicular to the surface and parallel to each other.

Investigation has revealed that the molecules of these oriented films are arranged so that their polar portions go into solution, while the insoluble portion tends to float above the surface of the water. Oriented films of this type exhibit various properties, which can be qualitatively observed and quantitatively measured. For example, they may be mechanically compressed, and this produces several readily observable effects. If the expanded film is subjected to compression by a movable barrier, it will exhibit a series of colors (yellow, gold, red-purple, blue, and green) as the compression is increased. On further compression, the color spectrum will be repeated four or more times until a limiting compression value is reached when the film again becomes colorless.

Many quantitative measurements have been made of the properties of mono-molecular films formed by the even- and odd-numbered-carbon acids from  $C_{12}$  to  $C_{26}$ . When spread on the surface of distilled water at a constant temperature of  $20^{\circ}\text{C}.$ , all of the saturated fatty acids exhibit essentially similar behavior with respect to the compressibility of their films. At areas greater than about  $21 \times 10^{-16}$  sq.cm. per molecule, there is little or no measurable resistance to pressure. At this point there is observed a sudden opposition to further contraction, and the compressing force increases practically linearly with decreasing area up to the point at which the film collapses as a result of piling up of the molecules of the film.

The observations may be interpreted as evidence that when the area of a film of saturated fatty acids has been reduced to the extent where the molecules are closely packed together, the area occupied per molecule is  $21 \times 10^{-16}$  sq.cm. and is inde-

pendent of the length of the carbon chain. The fact that the molecules occupy the same area independent of the length of the carbon chain, and the fact that the area formed is the area of the cross section of a methylene group determined in other ways, is conclusive proof of the orientation of the molecules of fatty acids producing the film. It is evident, therefore, that because of the affinity of the hydrocarbon portion of the molecules for each other, the molecules spread on the surface of the water only far enough for their heads or hydrophilic parts to come in contact with water. The surface tension of the water, therefore, is not decreased unless enough fatty acid is added

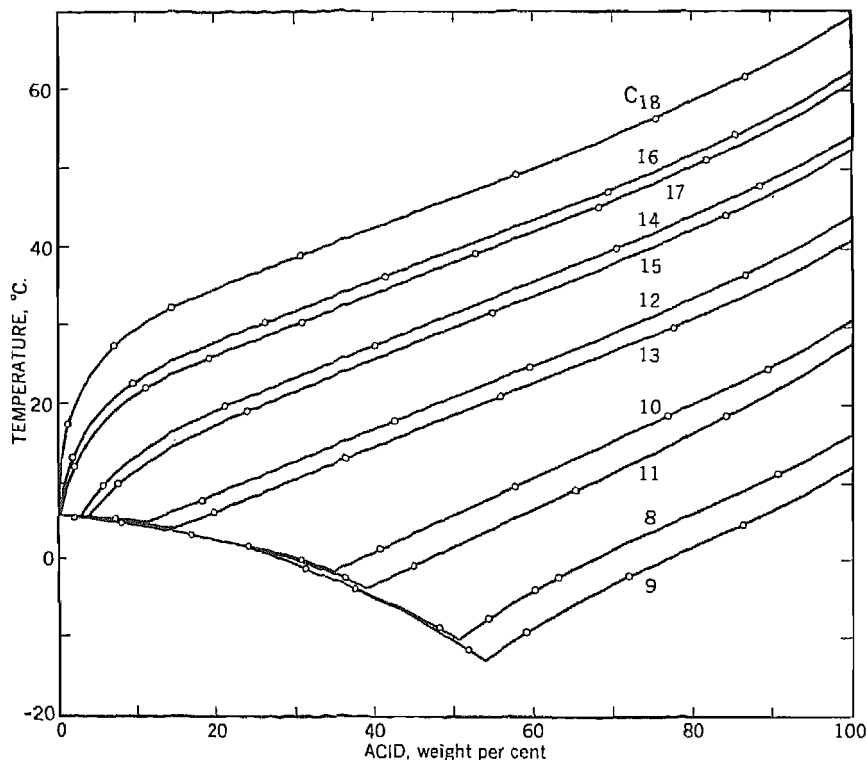


Fig. 9. Solubilities of saturated fatty acids from pelargonic to stearic in anhydrous benzene (30).

to cover the surface completely with a monomolecular film. By measuring the volume of fatty acid required to form a monomolecular film covering a given area, the thickness of the film can be calculated. Also, by placing a known number of molecules on the surface and measuring the area to which the film spreads before the surface tension becomes that of pure water, the area per molecule can be measured. See *Surface-active materials*.

**Nonaqueous Systems.** Solubility data for the lowest members of the fatty acid series in a wide variety of organic solvents are available, and complete phase diagrams for many of these systems have been constructed. Numerous investigations dealing with systems composed of one or more of the first six members of the series and various organic solvents have been reported and the data have been compiled by Seidell (31). Data on the solubilities of solvent-acid systems from caprylic to stearic acid are due almost entirely to the efforts of Ralston and co-workers (16,17,30), who determined the

solubilities of 11 fatty acids ( $C_9$ - $C_{18}$ ) in 23 organic solvents, including aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, alcohols, ketones, glacial acetic acid, esters, nitroparaffins, 1,4-dioxane, and furfural. The fatty acids used in the solubility determinations were of relatively high purity judged by their freezing points. The solubilities were generally measured either from  $0^\circ\text{C}$ ., or from the freezing point of

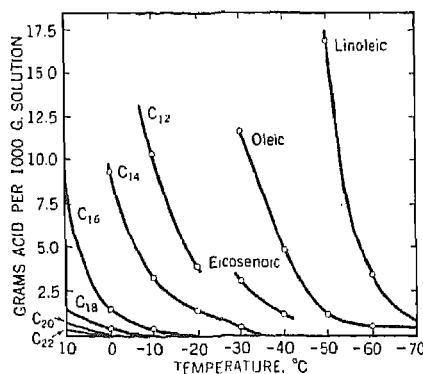


Fig. 10. Solubilities of some saturated and unsaturated fatty acids in petroleum naphtha (12).

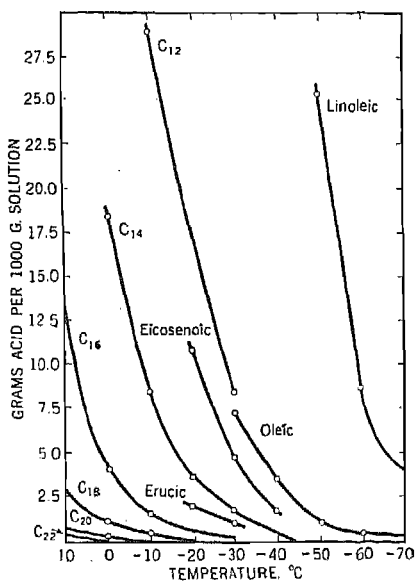


Fig. 11. Solubilities of some saturated and unsaturated fatty acids in methanol (12).

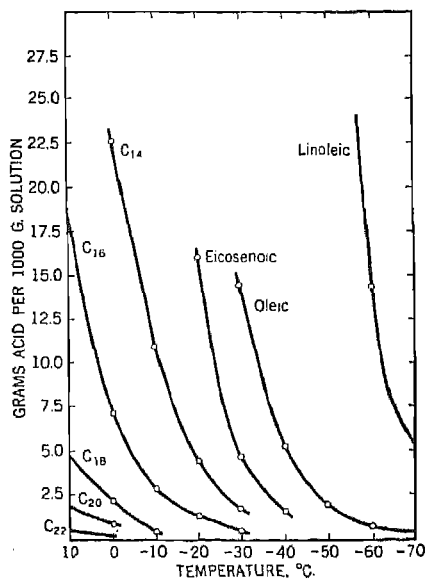


Fig. 12. Solubilities of some saturated and unsaturated fatty acids in acetone (12).

the solution, to  $100^\circ\text{C}$ . in the case of solvents boiling above this temperature. A typical family of solubility curves obtained by Ralston, *et al.*, are shown in Figure 9. The solubility curve of an even-numbered-carbon acid lies above the curve of the next higher odd-numbered-carbon acid throughout all, or a considerable part, of the temperature range. The even- and odd-numbered acids, therefore, form two distinct solubility series.

**Solubility of Fatty Acids at Low Temperatures.** Because of the utility of low-temperature-solvent crystallization processes for laboratory and technical preparation of fatty acids and esters, Foreman and Brown investigated the solubility behavior of a number of higher fatty acids in several solvents at +10 to  $-70^{\circ}\text{C}$ . (see Figs. 10, 11, and 12). Because of the long time required to establish equilibrium at the lower temperature, the solid and solvent were stirred for an arbitrary period of ten hours at the selected temperature before determining the solubility. Solubility values obtained by approaching the selected temperature from the warm side were found to be approximately 10% higher than those obtained by approaching it from the cold side. However, in low-temperature crystallization, a solution of fatty acids is generally cooled to effect separation of a specific component; consequently, the determinations were made in this manner rather than by warming to a higher temperature. Foreman and Brown also determined the solubility ratios of several pairs of fatty acids in various solvents (see Table VIII). For a detailed treatment of the solubility of fatty acids, see reference (8a).

TABLE VIII. Solubility Ratios of Some Fatty Acids.

Solvent	Temp., $^{\circ}\text{C}$ .	Oleic, %	Palmitic, %	Ratio, oleic: palmitic
Methyl acetate	-25	10.0	0.74	14.7
Acetone	-30	14.2	0.48	30.0
Methanol	-30	7.08	0.20	35.4
Butyl alcohol	-25	62.8	1.32	47.6
Ethylidene dichloride	-25	26.8	3.24	82.7
Petroleum naphtha	-30	11.8	0.09	130.0
Carbon disulfide	-30	15.7	<0.1	>157.0
Toluene	-30	50.2	<0.1	>500.0
Ethyl ether	-40	43.7	<0.1	>450.0
		Linoleic, %	Oleic, %	Ratio, linoleic:oleic
Petroleum naphtha	-70	0.60	0.24	2.5
Carbon disulfide	-62	4.12	0.398	10.3
Methanol	-70	3.94	0.32	12.3
Acetone	-70	5.19	0.40	13.0

Source: reference (12).

**Solubility of Binary Mixtures of Fatty Acids.** The technique of fractional crystallization from solvents for the resolution of mixtures of fatty acids is of fundamental importance in the analysis of fats and the laboratory preparation of pure fatty acids, and recently it has assumed considerable industrial importance. Data for the solubility of single acids are of limited value in predicting the behavior of mixtures of these substances in solution because of the intersolubilizing effects of different components of a given system of acids and solvent. Relatively few systematic phase investigations of such solutions have been made, which is attributable in part to the experimental difficulties in equilibrating and separating mixtures of fatty acids and volatile solvents at relatively low temperatures.

The only investigations reported to date covering the composition of the solid and liquid phases existing in equilibrium in ternary systems composed of two fatty acids and a solvent are those of Singleton (33). The systems are oleic-stearic-acetone, oleic-stearic-hexane, oleic-palmitic-acetone, and oleic-palmitic-hexane, at temper-

atures of 0, -10, -20, -30, and -40°C. Complete phase diagrams for each system and each temperature have been constructed and show that the intersolubilizing effect of oleic acid on either palmitic or stearic acid is greater in commercial hexane than in acetone, and also that oleic acid of high purity can be obtained from a mixture of this acid with either stearic or palmitic acid by selecting the proper conditions for crystallization.

Figure 13 represents the compositions of the liquid and solid phases in equilibrium when varying proportions of oleic and stearic acids in commercial hexane are cooled to a

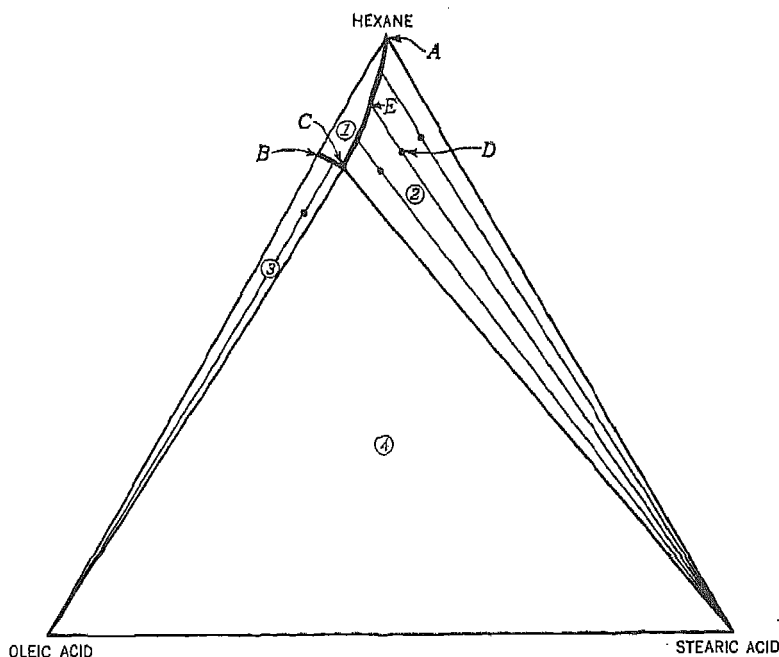


Fig. 13. Solubilities of oleic and stearic acids in commercial hexane.

temperature of -20°C. The point *A* represents the solubility of stearic acid in commercial hexane (about 0.0005%), *B* represents that of oleic acid (8.999%), and *C* represents the composition of a solution in equilibrium with *both* stearic and oleic acids. This solution contains approximately 0.12% stearic acid. Area 1 represents a single-phase solution. Any mixture whose composition falls in area 2, such as *D*, will at -20°C. yield stearic acid and a solution whose composition is indicated by the intersection of the tie line, *DE*, with the boundary of the single-phase area. A mixture in the narrow area 3 will yield oleic acid and a solution of composition between *B* and *C* determined by the intersection of a tie line from the oleic acid corner of the diagram with the boundary of area 1. In area 4, mixtures separate into two solid phases, stearic acid and oleic acid, and solution of fixed composition *C*.

#### SURFACE TENSION

Despite the availability of equipment, the simplicity of the determination, and the utility of surface- and interfacial-tension data, relatively few systematic measurements

have been reported for these properties of the fatty acids and esters. Typical of the meager data of this type to be found in the literature are those compiled in Table IX.

TABLE IX. Surface and Interfacial Tension of Typical Fatty Acids and Esters.

Compound	Temp., °C.	Surface tension against air, dynes/cm.	Interfacial tension against water, dynes/cm.
Eranthic acid.....	20	28.31	7.00
Caprylic acid.....	18.1	28.82	8.217
Undecylic acid.....	25	30.64	10.14
Oleic acid.....	20	32.50	15.59
Ricinoleic acid.....	16	35.81	14.25
Ethyl caproate.....	20	25.81	19.80
Ethyl pelargonate.....	20	28.04	23.88
Ethyl oleate.....	20	—	21.34

Source: p. 233 of reference (6).

The surface tension of the fatty acids decreases with increasing temperature and reaches zero at the critical temperature. For the greater part of the temperature range, the relation between surface tension and temperature is nearly linear. The interfacial tension at the phase boundary is generally influenced more by the presence of impurities than is the case with surface tension. Because of this fact and the failure to use highly purified products, the reported values for the surface and interfacial tensions of fatty acids and esters are not always trustworthy.

The surface tensions of the fatty acids in the liquid state are related to their densities and molecular weights by the equation  $P = M\gamma^{1/4}/(D - d)$ , where  $M$  is the molecular weight,  $\gamma$  is the surface tension,  $D$  and  $d$  are the densities of the acids in the liquid and vapor states, respectively, at the same temperature, and  $P$  is the parachor relating the surface tension to the molecular volume. The parachor equation defines the molecular volume of an acid at unit surface tension and makes possible the intercomparison of molecular volumes at points where the surface tensions are identical. The values of the surface tensions and parachors for various fatty acids are given in Table X.

TABLE X. Surface Tension and Parachor Values of Various Fatty Acids.

Acid	Surface tension, at:		Parachor value, at:	
	90°C.	95°C.	90°C.	95°C.
Oleic.....	27.94	27.52	765.07	766.93
Elaidic.....	26.56	26.31	760.44	764.93
Stearic.....	26.99	26.42	777.79	778.87
Erucic.....	28.56	27.77	932.40	938.91
Brassicic.....	27.40	27.28	929.29	934.36
Behenic.....	37.77	37.61	950.07	951.36

Source: reference (32).

#### ELECTRICAL PROPERTIES

The important electrical properties of the fatty acids include equivalent conductance, specific conductance, and specific inductive capacity or dielectric constant. The equivalent and specific conductances are measures of the capacity to conduct an elec-

trical current. The former is measured in solution, generally water, and the latter in the liquid or solid state.

**Dissociation and Equivalent Conductance.** The values of  $K$  for the normal fatty acids have been determined only for the series formic to pelargonic, because the solubility of the acids in water is very slight with chain lengths above  $C_9$  (see p. 186). Dissociation constants and equivalent conductances of the lower acids are shown in Table XI.

TABLE XI. Dissociation Constants,  $K$ , and Equivalent Conductances,  $\Lambda_0$ , for Saturated Fatty Acids in Aqueous Solutions at 25°C.

Acid	$K \times 10^5$	$\Lambda_0$
Formic.....	21.0	404
Acetic.....	1.813	390.8
Propionic.....	1.32	386
Butyric.....	1.50	383
Valeric.....	1.56	381
Caproic.....	1.40	379
Enanthic.....	1.30	378
Caprylic.....	1.41	377
Pelargonic.....	1.1	377

Source: reference (21).

**Specific Conductances.** Only a few determinations have been made of the specific conductances of the higher fatty acids. Lederer and Hartleb determined the specific conductances of caproic, myristic, and palmitic acids, and of technical stearic (m.p. 56°C.) and oleic acids (23). Measurements were made on the liquid acids at various temperatures between 100 and 200°C. and the results extrapolated to the melting- and boiling-point temperatures. At 158–160°C.,  $\lambda \times 10^{11}$  was: caproic, 21.5; myristic, 11.8; palmitic, 10.3; stearic, 7.3; and oleic, 26. They also calculated the temperature coefficients of conductivity. The specific conductance of the higher fatty acids decreases with increasing chain length in correspondence with the well-known decrease in the strength of the acids and corresponding ease of hydrolysis of their salts as the series is ascended. The marked increase in conductivity of oleic acid compared with stearic acid is in accord with the observation that the salts of the higher unsaturated fatty acids are more strongly dissociated and therefore better conductors than those of the saturated acids of the same chain length.

It has been observed that the curves for the temperature plotted against the logarithm of the coefficient of electrical conductivity of fused salts are generally linear in form. This is apparently only partly true for the higher fatty acids since Lederer and Hartleb found that plots of the logarithm of the conductivity against the temperature for these acids were linear up to about 140°C., but above this temperature they tended to become concave to the temperature axis.

**Dielectric Constant.** In general, the dielectric constants of the fatty acids decrease with increasing molecular weight, but in any case they are not large, ranging from 6 to 7 for the lower acids and esters and from 2 to 5 for the higher members of the series. Formic acid is an exception, as is glyceryl triacetate (18).

#### HEATS OF FORMATION AND COMBUSTION

Practically all of the available information on the heats of formation and combustion of the higher fatty acids and their derivatives is due to the work of Stohmann and



his co-workers during the 1890's. Kharasch critically reviewed the literature on the heats of combustion of organic compounds and compiled a table of "best" values available up to 1929 (see Table XII). Because of this selection, a much higher degree of correspondence is indicated between the experimental and calculated values for the fatty acids than would otherwise be expected on the basis of the probable purity of the acids generally available at the time that many of the measurements were made. Kharasch's values are expressed in absolute kilojoules (at constant pressure) per gram-molecular weight of substance *in vacuo* and in kilogram-calories at 15°C., but values contained in the *International Critical Tables* are expressed in 1922 International Combustion Calories per gram formula weight (*in vacuo*) in the liquid state, when combustion is carried out at constant pressure of 1 atm. and at 18–20°C. to form gaseous carbon dioxide and liquid water.

TABLE XII. Heats of Combustion of Saturated Fatty Acids and Esters.

Acid	Acid	Heat of combustion at 15°C., kg.-cal.		
		Methyl ester	Ethyl ester	Triglyceride
Formic.....	62.8	233.1	391.7	—
Acetic.....	209.4	381.2	539.9	—
Propionic.....	367.2	552.3	690.8	—
Butyric.....	524.3	692.8	851.2	1941.1
Valeric.....	681.6	—	1017.5	2308.6
Caproic.....	831.0	—	—	5706.3
Enanthic.....	986.1	—	—	6650.3
Capric.....	1458.1	—	—	10264.7
Undecylic.....	1615.9	—	—	—
Lauric.....	1771.7	—	—	—
Myristic.....	2085.8	—	—	—
Palmitic.....	2398.4	—	—	—
Stearic.....	2711.8	—	—	—
Arachidic.....	3025.9	—	—	—
Behenic.....	3338.4	—	—	—

Source: reference (22).

TABLE XIII. Comparative Heats of Combustion of Some Corresponding Saturated and Unsaturated Fatty Acids.

Acid	Formula	Saturation	Heat of combustion at 20°C., kg.-cal.	
			Exptl.	Calcd.
Undecanoic	$C_{11}H_{22}O_2$	Saturated	1615.9	1615.1
10-Undecenoic	$C_{11}H_{20}O_2$	1 double bond	1579.7	1576.0
10-Undecynoic	$C_{11}H_{18}O_2$	1 triple bond	1537.8	1544.0
Stearic	$C_{18}H_{36}O_2$	Saturated	2711.8	2709.2
Oleic (cis)	$C_{18}H_{34}O_2$	1 double bond	2681.8	2663.6
			2657.0	
Elaidic (trans)	$C_{18}H_{34}O_2$	1 double bond	2664.2	2670.1
Stearolic	$C_{18}H_{32}O_2$	1 triple bond	2628.6	2638.1
Behenic	$C_{22}H_{44}O_2$	Saturated	3338.4	3334.4
Erucic (cis)	$C_{22}H_{42}O_2$	1 double bond	3296.7	3295.3
Brassicidic (trans)	$C_{22}H_{42}O_2$	1 double bond	3290.1	3288.8
Behenolic	$C_{22}H_{40}O_2$	1 triple bond	3254.9	3263.3

Source: p. 158 of reference (6).

The values for the heats of combustion of some corresponding monoethenoid, monoethynoid, and saturated acids are given in Table XIII. Both the experimental and calculated values for the heat of combustion of oleic acid are not in accordance with the rule that a *cis* isomer should possess a higher heat of combustion than the *trans* isomer, but, despite considerable additional work since the values for oleic and elaidic acids were first reported, the heats of combustion for these acids are not accurately known. However, except for the lower value reported by Kharasch, the values reported for oleic acid are higher than for elaidic acid, which is in accordance with other known facts concerning the relative stabilities of these two acids. Following the development of more rigorous methods of purifying oleic acid, Keffler prepared a series of esters of oleic and elaidic acids and determined their heats of combustion (19). In each case, the oleate was found to have the higher heat of combustion, and the average isothermal heat of transition from oleate to elaidate was found to be about +1.6 kg.-cal. per mole.

### Spectral Properties

When radiation of any frequency in the spectroscopic portion of the electromagnetic spectrum strikes a material medium it will be either transmitted through the medium, reflected from one of the surfaces, or absorbed. Absorption can occur only if within the molecule upon which the radiation falls there is a resonator whose natural period of oscillation coincides exactly with a particular frequency of the radiation. The relation between the frequency,  $f$ , and the energy,  $E$ , of radiation is given by Planck's law,  $E = hf$ , where  $h$  is the universal Planck's constant. In the ultraviolet and visible portion of the spectrum the frequencies are associated with energies of the same order of magnitude as those involved in changes in the electronic state of the molecule. It has been shown that most absorption bands in these regions may be characterized by transitions from the normal homopolar (nonionic) state,  $N$ , to the ionic excited state,  $V_1$ , which may be represented as  $N \rightarrow V_1$ . Frequencies of radiation in the infrared region are associated with lower energies only sufficient, generally, to coincide with the energies involved in vibrational changes (near infrared) and rotational changes (far infrared). See also *Spectroscopy*.

From these observations it can be readily understood why a study of the radiation absorbed as a function of the frequency can have wide application in the characterization of fatty acid compounds, in the control of their isolation and purification procedures, in the determination of their molecular structures, and in their qualitative and quantitative analysis.

The spectroscopic portion of the electromagnetic spectrum includes radiation above about  $0.05 \mu$  (500 Å.) where the vacuum ultraviolet overlaps the region of soft x-radiation, to about  $1000 \mu$  (10,000,000 Å.) where the far infrared region overlaps the lower Hertzian region (microwaves or radar waves). The various subdivisions of this portion of the electromagnetic spectrum and the type of oscillations associated with each division and subdivision are given in Table XIV. Some investigations of the spectral properties of the fatty acids have been made in almost all of these divisions, and applications of these spectral properties to the solution of problems in fatty acid chemistry are increasing rapidly as methods for measuring absorption are being simplified.

The direct-reading spectrophotometer is now most commonly employed for all

these measurements. Throughout all the various divisions of the spectrum this instrument is essentially the same. Modifications are required in the selection of the source to provide the required radiation, of the optics to provide media transparent to the selected radiation, and of the detector to provide suitable sensitivity to the radiation selected. These factors, together with the types of oscillations within the molecule, are responsible for the divisions and subdivisions of the electromagnetic spectrum. They are listed for each subdivision in Table XIV. A scale, which illustrates the relative magnitudes of the various subdivisions of the spectroscopic portion of the electromagnetic spectrum and which provides a means for interconversion of the various units commonly used to express frequency, wave number, and wave length, is given in Figure 14.

TABLE XIV. The Spectroscopic Portion of the Electromagnetic Spectrum.

Spectrum division	Wave length region	Rotator	Source of radiation	Prism material	Detector
Infrared:					
Far	1000-25 $\mu$	Molecular rotations	Globar	Gratings (above 40 $\mu$ ); thallium bromide (40-25 $\mu$ )	Radiometer, bolometer, thermopile
Near	25-0.75 $\mu$	Molecular vibrations	Nernst glower	Glass (0.75-3.5 $\mu$ ); lithium fluoride (3.5-6 $\mu$ ); calcium fluoride (6-9 $\mu$ ); sodium chloride (9-15 $\mu$ ); potassium bromide (15-25 $\mu$ )	Radiometer, bolometer, thermopile
Visible	750-400 $m\mu$	Outer electrons	Tungsten filament	Glass	Photoelectric cell
Ultraviolet:					
Near	400-320 $m\mu$	Outer electrons	Hydrogen discharge	Quartz	Photoelectric cell
Far	320-220 $m\mu$	Outer electrons	Hydrogen discharge	Quartz	Photoelectric cell
Vacuum	220-50 $m\mu$	Inner electrons	High-voltage spark	Lithium fluoride (to 100 $m\mu$ ); gratings (below 100 $m\mu$ )	Sensitized photographic plates

The groupings within the molecule responsible for absorption are called chromophores, that is, color producers, a term used for ultraviolet and infrared absorption as well as for visible absorption groups responsible for color. Lists of the chromophoric groups most commonly encountered in a study of the spectral properties of fatty acids, their esters and glycerides are given in Table XV.

**Infrared Absorption.** The far infrared region has recently received increased attention as a result of the introduction of synthetic materials for prisms which transmit radiation satisfactorily to about 40  $\mu$ . This region has been investigated only as a subject of spectroscopic research and no applications or investigations of the fatty acids have as yet been made.

The near infrared absorption spectrum of a molecule has been called the molecule's fingerprint. Until recently measurements in this region were made by techniques which required considerable specialized skill and were, moreover, both cumbersome and time-consuming. The introduction of direct-reading instruments and improved electronic devices has resulted in the accumulation of considerable data on the near infrared absorption of organic compounds. However, in the field of the fatty

acids and related compounds there is still need for the collection of many more "finger-prints" before the full utilization of this branch of spectrophotometry can be realized.

The infrared spectra of the methyl, glycol, and glycerol esters of unsaturated  $C_{18}$  fatty acids, including the triene-conjugated elcostearic acid, have been measured from  $2\ \mu$  to  $12\ \mu$  (45). Absorption bands were observed at  $3.5\ \mu$ ,  $5.8\ \mu$ ,  $6.9\ \mu$ ,  $8.4\ \mu$ ,  $10.0\ \mu$ , and  $11.5\ \mu$ . (Compare Table XV.) The band at  $8.4\ \mu$  was attributed to an unidentified oxygen linkage on the basis of the increase in its intensity in the order methyl-glycol-glycerol. Experiments with deuterium-substituted fatty acids have shown that it very probably arises from a deformed hydroxyl band (48). The greater intensity of the band at  $10.0\ \mu$  in the spectra of the conjugated elcostearic acid led to the assignment of this band to conjugated ethylenic linkages. Note, however, no. 20 in Table XV, which may account for the appearance of this band in many nonconjugated esters. No explanation was offered for the appearance of the band at  $11.5\ \mu$  (note, however, Table XV, no. 21) nor for the nonappearance of a band just above  $6.0\ \mu$ , attributable to the single ethylenic group. Other studies of the infrared spectra of the ethyl esters of several unsaturated fatty acids over the limited range  $5.2$ – $6.8\ \mu$  (57) have revealed an intense band at about  $6.0\ \mu$  for ethyl oleate, linoleate, and linolenate, all considered to have the all-cis isomeric configuration. A similar band for the ethyl esters of elaidic and linolelaidic acids, the all-trans isomers, was considerably weaker. Hence, spectral properties afford a means of differentiating between cis and trans forms of the fatty acids.

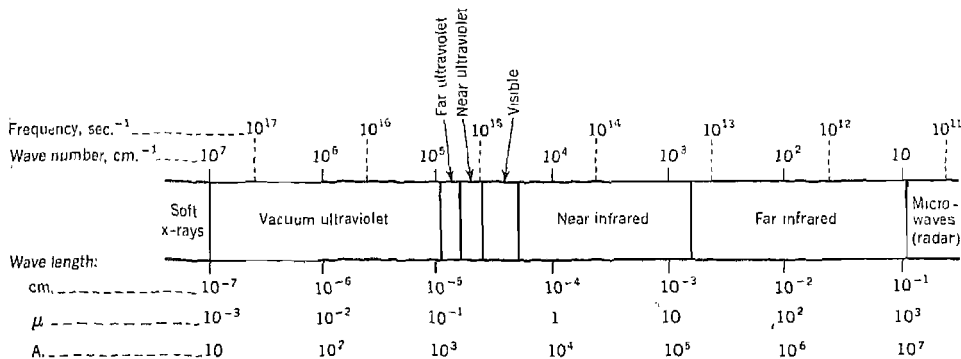


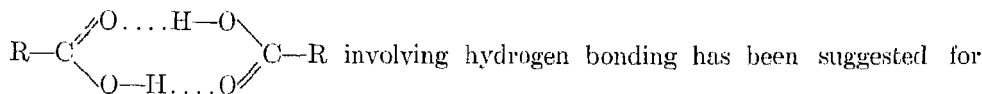
Fig. 14. The spectroscopic portion of the electromagnetic spectrum.

The infrared absorptions of methyl oleate and methyl elcostearate have been measured before and after exposure to ultraviolet light (45). The observed shift from  $3.4\ \mu$  to about  $3.1\ \mu$  was attributed to the formation of free hydroxyl groups (Table XV, no. 3).

The appearance of absorption attributable to the hydroxyl group (Table XV, no. 3) in some saturated fatty acids and its complete absence in others, particularly the lower members of homologous series, has been the subject of a detailed study of their infrared absorption in the vapor phase (48). Measurements of these compounds at  $139^\circ\text{C}$ ., a temperature where they are known to be monomers (97% dissociation), and at  $24^\circ\text{C}$ ., where dimers are present (9% dissociation), reveal the fact that the non-appearance of the hydroxyl absorption results from dimer formation. The structure

TABLE XV. Chromophoric Groups and Raman Frequencies of Special Interest in the Study of the Spectral Properties of Fatty Acids.

Infrared chromophores			Ultraviolet chromophores		
No.	Functional group	Wave length of maxima (approx.), $\mu$	No.	Functional group	Wave length of maxima (approx.), $m\mu$
1	$\begin{array}{c}   \\ -C-O \\   \end{array}$	1.2	23	$\begin{array}{c}   \quad   \\ -C=C- \\   \quad   \end{array}$	180
2	$\begin{array}{c}   \\ -C=O \\   \end{array}$	1.4	24	$-COOH$	200
3	$-O-H$	2.8	25	$-COOR$	200
4	$\begin{array}{c}   \\ =C-H \\   \end{array}$	3.2	26	$(C\equiv C)_2$	232
5	$-O-H-O-$	3.2	27	$(C\equiv C)_3$	268
6	$-CH_3$	3.5	28	$(C=C)_1$	310
7	$\begin{array}{c}   \\ -CH_3 \\   \end{array}$	3.5	29	$\begin{array}{c}   \\ -(C=C)C=O \\   \end{array}$	232
8	$\begin{array}{c}   \\ -C-H \\   \end{array}$	3.5	30	$\begin{array}{c}   \\ -(C=C)_2C=O \\   \end{array}$	268
9	$-O-D$	3.8	31	$\begin{array}{c}   \\ -(C=C)_3C=O \\   \end{array}$	310
10	$-O-D-O-$	4.4	32	$-C=O$	280
11	$\begin{array}{c}   \\ -C=O \\   \end{array}$	5.5-6.5	Raman frequencies		
12	$-COOR$	5.8	No.	Functional group	Frequency shift (approx.), $cm^{-1}$
13	$-COOH$	5.9			
14	$\begin{array}{c}   \quad   \\ -C=C- \\   \quad   \end{array}$	6.2	33	$\begin{array}{c}   \quad   \\ -C-C-(\text{aliphatic}) \\   \quad   \end{array}$	800-1000
15	$-CH_2$	6.9		$\begin{array}{c} R \\   \\ R-C=CH_2 \end{array}$	1644
16	$-CH_3$	6.9	34	$\begin{array}{c}   \quad   \\ -C=C- \\   \quad   \end{array}$	1650
17	$-O-H$	8.5	35	$-C=C- (cis)$	1670
18	$\begin{array}{c}   \quad   \\ -C-O-C- \\   \quad   \end{array}$	9.0	36	$-C=C- (trans)$	1700
19	$-O-H$	9.5	37	$-COOH$	1700
20	$RCH=CHR (trans)$	10.2	38	$-COOR$	1700
21	$\begin{array}{c} R \\   \\ R-C=CHR \end{array}$	11.9-12.7	39	$-C=O$	1720
22	$RCH=CHR (cis)$	14.0-14.6	40	$-C\equiv C-$	2035
			41	$-C\equiv C-$	2233
			42	$-CH_3$	3000
			43	$-O-H-O-$	3000-3600
			44	$\begin{array}{c}   \\ -C-H \\   \end{array}$	3010
			45	$-O-H$	3400



involving hydrogen bonding has been suggested for dimer formation from electron diffraction studies. The detection of hydrogen bonding is an early achievement of infrared spectroscopy. The absence of the free hydroxyl band can be interpreted as infrared support for this structure of dimer formation.

Comparisons of fatty acids containing deuterium have been made to account for the complete disappearance of the hydroxyl band upon dimer formation. With these deuterium compounds the intensity of the O—D band at  $3.77 \mu$  diminishes and that of the O—D—O band at  $4.35 \mu$  increases (Table XV, nos. 9 and 10) with dimer formation. With the hydrogen compounds the intensity of the free hydroxyl band at  $2.75 \mu$  de-

creases but no new band is observed. However, the —C—H band at  $3.2 \mu$  (Table XV, nos. 3 and 4) is observed to increase. This increase is interpreted to result from the superposition of the new O—H—O band at  $3.2 \mu$  (Table XV, no. 5). These studies also illustrate how infrared measurements can be used to obtain heats of dissociation, force constants, bond distances, and bond strengths.

Investigations have been made in the very near infrared of the hydroxyl-like bands at  $1.18 \mu$  and  $1.4 \mu$  (44). The groups responsible for these bands are still somewhat in doubt. Recent work has shown that they probably do not arise from hydroxyl groups, but from C—O and C=O, respectively (Table XV, nos. 1 and 2).

Barnes *et al.* investigated the infrared absorption of 363 synthetic and natural compounds including a few fatty acids and related compounds and have prepared a library of representative absorption curves (35). The range covered was only from about  $5 \mu$  to  $13 \mu$ . Infrared data for other fatty acids, esters, glycerides, etc., are needed, together with more complete measurements on those compounds for which limited data have been obtained. See, however, the most recent papers (64,69a).

**Visible and Near Ultraviolet Absorption.** A chromophore which gives rise to absorption in the visible portion of the spectrum will cause the material to be colored. This is somewhat true also for most absorption in the near ultraviolet where characteristic maxima have end absorption crossing into the visible blue causing a complementary yellow color. As fatty acids, their esters, glycerides, etc., are entirely colorless, no absorption in the visible or near ultraviolet is expected. Actually most of these materials are very transparent in both of these regions. However, it should be pointed out that while the fatty acids do not absorb in these regions, many natural fats and oils exhibit selective absorption in both the visible and the near ultraviolet regions. In fact, absorption in these regions is of primary importance in the identification of the pigments of natural fats and oils and in the control or grading of the color of these materials.

**The Vacuum Ultraviolet and the Far Ultraviolet.** Below  $200 m\mu$ , the atmosphere absorbs radiation and the spectrograph must be evacuated. At about this region also, quartz becomes opaque and a fluorite or a lithium fluoride prism or a grating must be used. As both the technique and instrumentation of vacuum spectrophotometry are cumbersome, studies in the vacuum region have been confined to research problems. As may be seen from Table XV, it is in this region that most of the selective absorption of fatty acids would be found. Measurements have been extended to  $170 m\mu$  for a wide variety of saturated and unsaturated, conjugated and nonconjugated, and cis and trans fatty acids and esters (67). The results, in general, confirmed

the values given in Table XV. They showed a strong bathochromic effect of the ethylenic group for the all-trans isomer as compared to the all-cis form, also that the intensity of absorption in the vacuum ultraviolet increases sharply with increase in the degree of unsaturation.

Inspection of Table XV shows that with the exception of a few fatty acids, for example, eleostearic and parinaric, containing conjugated ethylenic linkages, no selective absorption of fatty acids occurs in the far ultraviolet region. However, many unsaturated fatty acids exhibit characteristic absorption bands at about 232  $m\mu$ , 268  $m\mu$ , and 320  $m\mu$ . This absorption has been called "preformed conjugation absorption" and was originally attributed to rearrangements to conjugated positions of the ethylenic linkages of the unsaturated fatty acids. However, recent work has shown that these bands are attributable to oxidation. The absorption at 232  $m\mu$ , 268  $m\mu$ , and 320  $m\mu$  may appear with some fine structure indistinguishable from that of eleostearic or parinaric acids, or it may be seen as a broad smooth band at these same wave lengths. The first type of "preformed conjugation" has been attributed to hydroperoxide formation followed by decomposition and dehydration to create an additional ethylenic group in such a position that it produces conjugation throughout the entire fatty acid molecule (69) (Table XV, nos. 26, 27, and 28). The second type of selective absorption caused by oxidation has been shown to be attributable to  $\alpha,\beta$ -unsaturated aldols and dienals formed by oxidation of the fatty acid to a hydroperoxide and followed by fission of the oxidized molecule (122) (Table XV, nos. 29, 30, and 31) (see p. 214). Summaries of "preformed conjugation" will be found in references (52,59).

Despite the lack of selective absorption in the limited region between 200-320  $m\mu$  (Fig. 14), known as the far ultraviolet, possibly 95% of the spectrophotometric investigations of fatty acids have been made in this area. This is due principally to the applications of a discovery that linoleic and linolenic acids are respectively isomerized to conjugated dienoic and to mixtures of conjugated dienoic and trienoic acids (Table XV, nos. 26 and 27) by heating with alcoholic potassium hydroxide, and that this isomerization is effected much more rapidly at higher temperatures, for example, with the use of a solution of alcoholic potassium hydroxide in ethylene glycol at 180°C. (42,53). This alkali-induced conjugation has been used as the basis for a direct spectrophotometric estimation of linoleic and linolenic acids in natural vegetable oils and has been extended to include arachidonic acid in animal fats and tallow (38,39,58) (Table XV, no. 28). A blanket of nitrogen to prevent further formation of preformed oxygen conjugation and means for applying the method in the presence of conjugated eleostearic acid have been suggested (50,60). Reviews of the use of alkali-induced conjugation as a direct spectrophotometric method for the estimation of fatty acids will be found in references (37,52).

The spectral properties of alkali-induced conjugation have been used to follow the fate of fatty acids during selective hydrogenation. It has been shown that partial hydrogenation of the linolenic acid in linseed oil produces an isomeric linoleic acid whose double bonds are not shifted to conjugated positions by heating with alkali (56). The use of spectral properties to follow the course of hydrogenation has been extended to other vegetable oils (43), and some isomeric conjugated fatty acids have been prepared using spectral measurements to control the isolation and purification procedure (65).

The natural occurring triene conjugation of  $\alpha$ -eleostearic acid has been used to

afford a direct spectrophotometric determination of this fatty acid in fresh tung oil (61), and was later extended to the simultaneous determination of both  $\alpha$ - and  $\beta$ -eleostearic acids (62). The technique has considerable advantages over the chemical method of calculation, from maleic anhydride addition, both in simplicity and in time consumed. The chemical method, moreover, is incapable of distinguishing between the two isomeric forms. As the relative amount of the  $\beta$ -isomer determines whether or not a tung oil may solidify in storage or shipment, determination of the ratio of  $\alpha$ - to  $\beta$ -eleostearic acid can be used to predict solidification of the oil.

Spectral properties have been used in numerous investigations to identify the products of oxidation and autoxidation of fatty acids (6,7). A lengthy series of technical papers has eliminated many possible compounds as responsible for the selective absorption of oxidized fatty acids (51). This absorption has recently been shown to arise from conjugation between the ethylene and carbonyl groups (122) (Table XV, nos. 29, 30, and 31).

Reviews of the applications of absorption in the far ultraviolet to studies of the fatty acids may be found in references (37,41,63,66). However, advances in this particular field of spectroscopy have been so rapid that only recourse to the most recent technical papers can provide the latest interpretations and applications of ultraviolet spectroscopy to fatty acid chemistry.

**Raman Effect** (*q.v.*). If the radiation which is reflected or scattered as it strikes a material medium is examined, it will be found to consist of three possible types known as: *Tyndall scattering*, *Rayleigh scattering*, and the *Raman effect*. The Raman effect differs from either Tyndall or Rayleigh scattering by virtue of the fact that no change occurs in the frequency of the incident radiation upon Tyndall or Rayleigh scattering, while in the Raman effect a series of scattered radiations is produced which differ in frequency from the incident radiation. Thus, if a monochromatic radiation is examined spectrographically, it is found upon scattering to be no longer monochromatic but rather is composed of the original frequency (from Tyndall and Rayleigh scattering) and new frequencies (from Raman effect). If the new frequencies are higher than the incident radiation, they are called anti-Stokes lines; if lower frequencies, Stokes lines. Stokes lines are, generally, considerably more intense and only they have practical importance.

The difference between the frequencies of the Stokes lines and the incident radiation is called the Raman frequency. It should be noted that a Raman frequency is a difference in frequency denoted by  $\Delta f$  and does not indicate a position in the electromagnetic spectrum. The Raman frequencies of a given substance are independent of the incident radiation.

A molecule can absorb infrared radiation only if the molecular vibration which exactly coincides with the frequency of the radiation causes a change in the dipole moment of the molecule. The selection rules from Raman effect, however, require a change in the molecular refractivity. Hence, Raman effect can both supplement and complement infrared data for the purpose of molecular structure determinations. Harrison has shown in detail how infrared and Raman effect can together constitute one of the most important tools for the determination of molecular structure (46).

A considerable collection of data on Raman frequencies has been compiled, particularly by Hibben, and is available in readily usable form for qualitative and quantitative purposes (49). Despite these accumulated data for organic substances, only little information has been collected on the Raman frequencies of fatty acids and



related compounds. Raman frequencies of particular significance in spectral studies of the fatty acids are included in Table XV. Application of the Raman effect to fatty acids has been discussed by Yvernault (70) who points out certain advantages over infrared absorption measurements.

Differentiation between *cis* and *trans* isomeric configurations has been one of the principal achievements of Raman spectroscopy. Studies of the ethylenic bond in fatty acids have established a frequency shift of about  $1650\text{ cm}^{-1}$  for the *cis* acids, oleic, ricinoleic, linoleic, etc.; and about  $1670\text{ cm}^{-1}$  for the corresponding *trans* forms, elaidic, ricinelaidic, linolelaidic, etc. (57,70). Furthermore, a characteristic C—H frequency at  $3010\text{ cm}^{-1}$  has about twice the intensity in *cis* compounds as in the corresponding *trans* compounds. The carboxyl frequencies in fatty acids (Table XV, no. 39) have also been investigated in some detail (54,55).

The use of Raman frequencies to identify and even quantitatively estimate the individual fatty acids in natural fats and oils has been suggested (47). Claims have been made that the saturated acids up to  $C_{11}$  can be identified by characteristic Raman frequencies.

Hydroxyl frequencies, hydrogen bond, and dimer formation have been investigated by Raman effect (36,68) with results which are in accord with infrared absorption studies. The hydrogen bond frequency overlaps the  $\text{—}\overset{\text{O}}{\underset{\text{H}}{\text{C}}}\text{—H}$  bond at  $2950\text{ cm}^{-1}$  in a manner analogous to the superposition of the  $\text{O—H—O}$  and  $=\text{C—H}$  in infrared measurements. Evidence for the carbon-to-carbon triple bond (Table XV, no. 41) in some animal fats and for a terminal double bond (Table XV, no. 34) in  $C_{10}$  fatty acids has been reported (70). Reviews of the applications of Raman effect to fatty acids will be found in references (6,7). (See *Spectroscopy; Raman effect*.)

### Crystal Properties

#### X-RAY INVESTIGATIONS

X-ray diffraction techniques have been helpful in classifying the physical and chemical behavior of fatty acids since certain of their properties are dependent upon the crystal structure, that is, upon the molecular arrangement in the solid. Most of our knowledge of the structure of long-chain hydrocarbons is of comparatively recent origin and is due to the work of Malkin, Müller, Piper, Shearer, Trillat, and a few others. For a discussion of the technique and interpretation of x-ray diffraction as applied to these compounds, the reader is referred to the papers of Müller (77), Shearer (84,85), Piper (79), Slagle (86), and Fankuchen (71).

The fatty acids and their related alcohols, esters, glycerides, and ketones have molecular structures characterized by parallel arrangement of the "zigzag" carbon

TABLE XVI. Axial Dimensions in Ångström Units and Angles of Inclination of Long-Chain Fatty Acids and Related Compounds.

Compound	Formula	a	b	c	$\beta$	ab	$\frac{ab}{\sin \beta}$	$\frac{c}{\sin \beta}$	$\frac{a}{\sin \beta}$	$\epsilon$
Lauric acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	9.76	4.98	36.9	$48^\circ 6'$	48.6	36.5	27.6	7.32	0.681
Stearic acid	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$	5.55	7.38	48.84	$63^\circ 16'$	40.94	36.6	43.76	4.95	0.671
Behenolic acid	$\text{CH}_3(\text{CH}_2)_7\text{C}:\text{C}(\text{CH}_3)_2\text{COOH}$	9.55	4.69	59.10	$53^\circ 30'$	44.76	36.0	47.51	7.67	0.612
Stearolic acid	$\text{CH}_3(\text{CH}_2)_7\text{C}:\text{C}(\text{CH}_3)\text{COOH}$	9.55	4.69	49.18	$53^\circ 4'$	44.76	35.8	39.28	7.63	0.614
Bromostearic acid	$\text{CH}_3(\text{CH}_2)_{11}\text{CHBrCOOH}$	11.04	4.90	52.88	$43^\circ 15'$	54.13	37.1	36.23	7.56	0.648

chains perpendicular or tilted with respect to the planes of maximum spacing formed by the terminal groups. In those cases in which the data have permitted structure

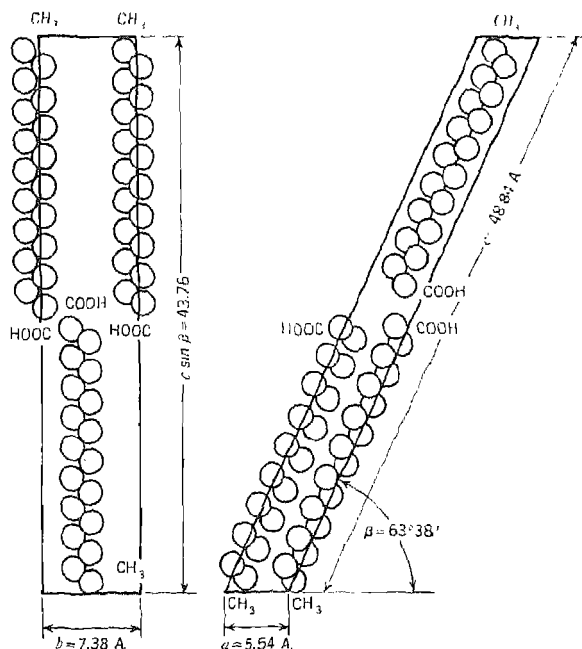


Fig. 15. A diagrammatic representation of the structure of stearic acid.

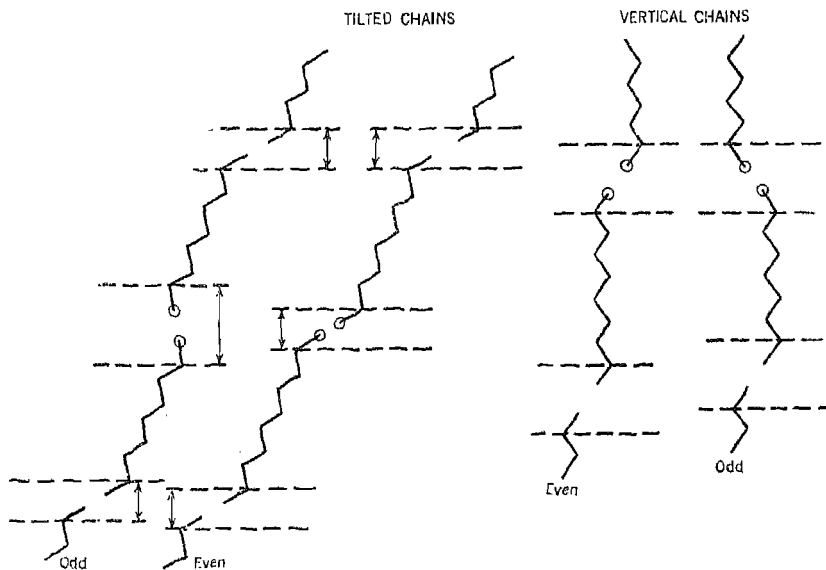


Fig. 16. Alternation in long-chain hydrocarbons.

determination, the fatty acids are monoclinic prismatic (Schoenflies,  $C_{2h}$ ; Hermann-Mauguin,  $2/m$ ) with four molecules in the unit cell (see *Crystals*). Table XVI gives

data collected by Hendricks (73). Figure 15 is a representation of the structure of stearic acid.

From consideration of the structures of long-chain compounds in general, the following generalizations may be made: (1) The unit cell contains two or four molecules, depending upon whether molecules lie "head-to-head" or "head-to-tail." (2) The measured increment in maximum spacing with each added methylene group may

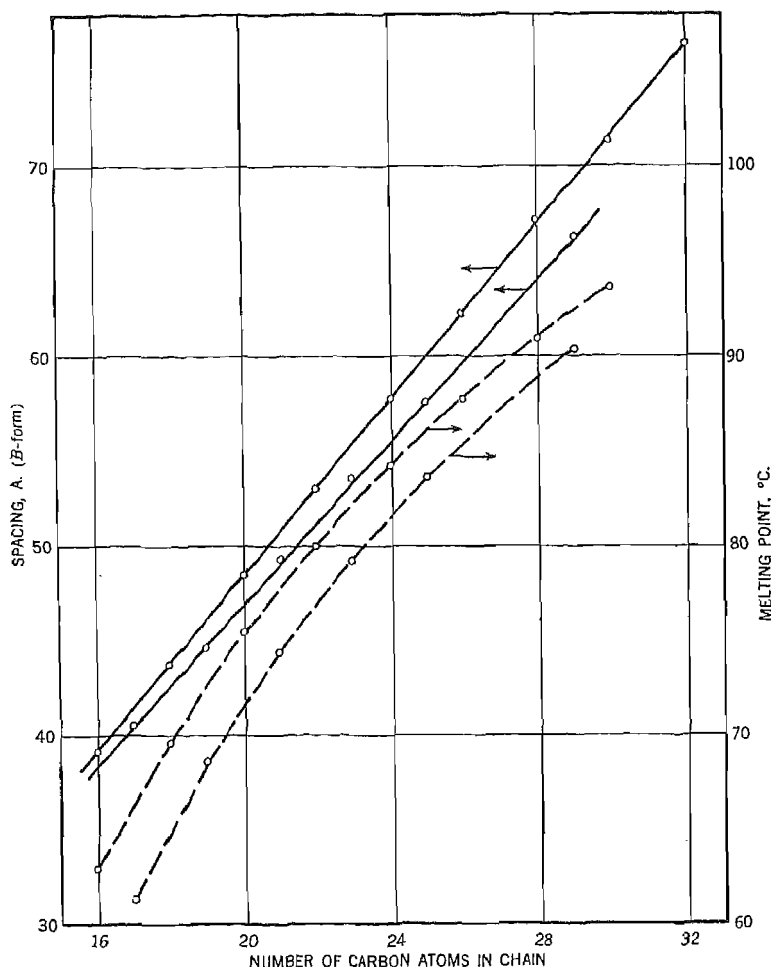


Fig. 17. Long-spacing and melting point alternation in long-chain compounds.

be either (a) about 1.3 Å., or (b) about 2.5 Å. (depending upon single- or double-chain length), or (c) values intermediate between these (depending upon the angle of inclination of the chain). (3) The long spacings measured by x-ray diffraction arise from the repetition of like planes populated by the chain ends. (4) The cross-sectional area for two hydrocarbon chains ( $ab \sin \beta$ ) is essentially constant and unaffected by dissimilarity of end groups.

The alternation of properties (or its absence) in long-chain compounds was satisfactorily accounted for by Malkin on the basis of structure (76). The terminal groups in odd-numbered carbon zigzag chains will be in *cis* positions while for even-numbered

chains they will be trans. This has essentially no effect in those cases (for example, hydrocarbons, alcohols, methyl esters) where the chains are vertical, for here the separation of successive chains is the same for even or odd chains. It is readily apparent from Figure 16 that in the case of tilted chains, however, there will be alternate terminal planes with greater separation in the case of odd-numbered chains. Since the same forces are required to act over these greater distances, the stability of the odd-numbered chains will be lower, and these will be expected to melt at lower temperatures than the even-numbered chains. The presence of the alternate terminal planes of different density should lead to an alternation in the long spacing (the distance between like planes populated by the chain ends) as the length of the tilted chain is increased. The resulting separate series of odd and even acids are shown graphically in Figure 17. This figure is based on the data of Francis and Piper (72), given more completely in Tables XVII and XVIII.

TABLE XVII. Long-Spacing Values of the Even-Numbered Normal Aliphatic Acids.

Carbon content of acid	Crystal spacings, Å.			
	Acid		Methyl ester	Ethyl esters (B-form)
	B-form	C-form		
14	—	31.60	—	—
16	39.1	35.60	43.45	—
18	43.75	39.75	47.95	25.80
20	48.45	44.15	52.30	—
22	52.95	48.3	57.02	29.90
24	57.75	52.6	61.70	32.15
26	62.2	56.25	66.15	34.45
28	67.15	61.05	70.80	36.65
30	71.4	65.2	75.25	38.75
32	76.3	69.25	79.95	41.1
34	80.5	73.3	84.15	43.45
36	85.25	78.1	89.30	46.3
38	90.0	82.1	93.00	48.05
46	108.2	99.05	121.7(?)	57.45

Source: reference (72).

TABLE XVIII. Long-Spacing Values of the Odd-Numbered Normal Aliphatic Acids.

Carbon content of acid	Crystal spacings, Å.		
	Acid (B-form)	Methyl ester	Ethyl ester
17	40.45	46.3	24.75
19	44.50	50.8	26.95
21	49.25	55.25	29.35
23	53.40	60.0	31.50
25	57.65	64.55	33.60
29	66.35	73.75	38.1

Source: reference (72).

Structural deductions based on long-spacing measurements, not requiring single crystals, have been useful in the study of long-chain compounds, although they do not permit detailed structure analysis. Figures 18–20 from Markley (6) illustrate the effectiveness of this method. Figure 18 is a reproduction of the diffraction patterns obtained from a series of fatty acids. Piper and Francis (72,79), and Pollard and co-

workers (81) discuss the use of this type of data in identification, analyses, and as a criterion of purity. Figure 19 compares patterns from the  $C_{22}$  acid, the corresponding alcohol, and the methyl and ethyl esters. The decrease in spacing (increased separation of lines in the pattern) and the disappearance of the odd-strong-even-weak

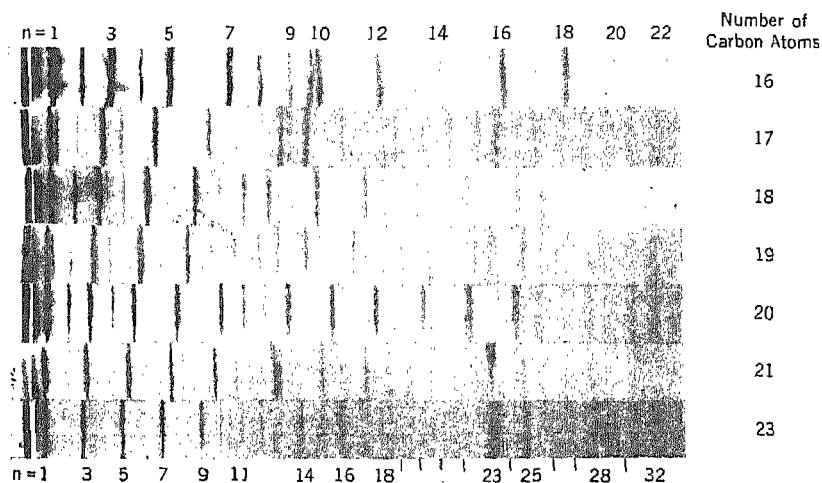


Fig. 18. Typical long-spacing diffraction patterns for a series of normal aliphatic acids (6).

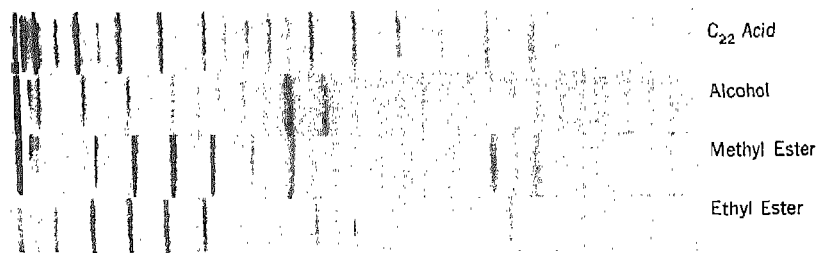


Fig. 19. Diffraction patterns obtained from  $C_{22}$  acid and corresponding derivatives (6).

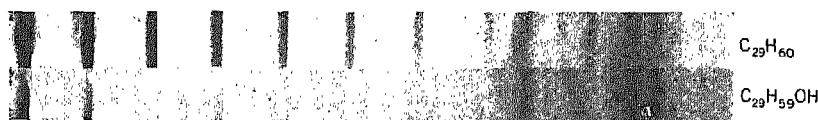


Fig. 20. The effect of side chain on x-ray diffraction patterns of long-chain compounds (6).

intensity distribution are evidence of the single-chain layer structure of the ethyl esters.

The presence of side-chain substituents such as oxygen and hydroxyl is indicated by another change in intensity distribution, illustrated in Figure 20. Saville and Shearer (83), using a nonrigorous method, showed that in ketones, for example, if the oxygen is attached at  $1/n$ th of the chain length, the  $n$ th,  $2n$ th,  $3n$ th, etc., orders of reflection will be weakened. This procedure has been used by Piper in the identification of 10-nonacosanol and by Velick in the study of tuberculostearic acid (80,87).

Chibnall, Piper, and numerous co-workers have made extensive studies of the

application of these techniques to the investigation of natural waxes; more recently Weitkamp (88) applied these techniques to wool scourings. Hendricks and Wildman (74), in addition, used characteristic (*hk*0) reflections in identification of material from *Cryptostegia* latex.

#### POLYMORPHISM

The ability of long-chain aliphatic compounds to form solid phases differing in crystal structure and in structure-dependent properties is of particular importance in the oil and fat industry, because the consistency, for example, of many products depends upon the particular polymorphic modifications present in the final form of the product. Each form can be characterized by its various properties such as melting point, resolidification point, heat of crystallization, specific volume, and x-ray diffraction pattern which will distinguish it from other forms of the same compound. The particular form assumed upon crystallization depends upon such factors as purity of the compound, the solvent from which it crystallizes, the presence or absence of particular crystalline nuclei, temperature, rate of cooling, and degree of supercooling.

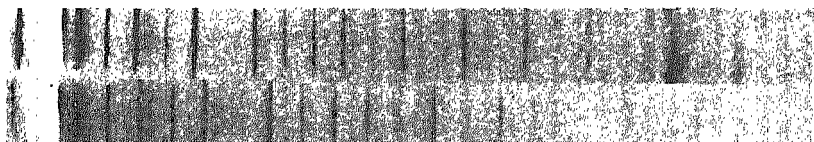


Fig. 21. X-ray diffraction pattern from *B*-form (upper) and *C*-form (lower) of stearic acid (6).

Markley (6) states that both reversible and irreversible polymorphism are to be observed in the monoesters of the fatty acids, while the acids themselves exhibit only the irreversible phenomena.

**The Normal Aliphatic Acids.** Francis and Piper (72) prepared and examined the even-numbered fatty acids from  $C_{14}$  to  $C_{38}$  and their methyl and ethyl esters and the odd-numbered acids from  $C_{17}$  to  $C_{29}$ . The even-numbered acids were obtained in two forms (*B* and *C*), differentiated according to their long-spacing values, the *B*-form having the higher long-spacing value. Table XVII includes these data and Figure 21 shows the characteristic differences of x-ray patterns of such polymorphic forms; the example is stearic acid. These workers state that the even-numbered acids crystallize from solvents in the unstable *B*-modification and are irreversibly converted to the *C*-form about  $5^{\circ}\text{C}$ . below their melting points. Generally, crystallization from hot glacial acetic acid will give the *C*-modification, while crystallization from benzene yields the longer-spacing *B*-form. Acids with an odd number of carbon atoms are reported to yield only the *C*-form on crystallization from solvents. The effect of the solvent on the form assumed on crystallization is open to some question. Markley states, in a private communication, that either form of stearic acid can be obtained from benzene at will by carrying out the crystallization above or below the transition temperature.

The polymorphism of the acids is apparently relatively simple, but with the esters, the situation is much more complex and, in spite of a great deal of work by many investigators, is not entirely clarified. Munford and Phillips (78) in investigations of the ethyl esters of the fatty acids from  $C_{12}$  upward find three distinct types of

polymorphic behavior: (1) *monotropy*, esters up to  $C_{16}$ , the  $\alpha$ -form of both even and odd numbers are metastable and unobtainable except in mixtures; (2) *monotropy and enantiotropy*, esters from  $C_{16}$  to  $C_{22}$ , the  $\alpha$ -forms of the odd numbers are stable near the melting point, but those of the even numbers have not been obtained; (3) *enantiotropy*, esters above  $C_{22}$ , the  $\alpha$ -forms of both even and odd numbers are stable near the melting point.

The x-ray data for the methyl and ethyl esters are included in Tables XVII and XVIII. For other data on the thermal properties of these compounds and the behavior of mixed systems see reference (6).

There is little information on the unsaturated acids though Lutton (75) has x-ray data on the two long-recognized forms of oleic acid. He reports the lower-melting form ( $13.3^{\circ}\text{C}.$ ) to be quite similar in structure to *B*- and *C*-forms of stearic acid (long spacing, 40.5 Å.; principle short spacing, 4.19 Å.). The higher-melting modification ( $16.2^{\circ}\text{C}.$ ) would seem to differ basically in structure, having a long spacing of 84.4 Å. (possibly 42.2 Å.) with a very irregular and unusual intensity distribution in the various orders, as well as two principle short spacings of 4.65 and 3.67 Å. For a detailed treatment of the occurrence of polymorphism and attendant phenomena in fatty acids, see reference (8a).

### Reactions

As typical aliphatic carboxylic acids, the fatty acids undergo the expected reactions (see *Acids, carboxylic*). In addition to the reactions characteristic of the carboxyl

TABLE XIX. Melting Points of Normal and Acid Salts of the Fatty Acids.

Cation	Salt, m.p., $^{\circ}\text{C}.$							
	Emanthate	Caprylate	Pelargonate	Laurate	Myristate	Palmitate	Stearate	Oleate
Ammonium (neutral) <sup>a</sup>	112	114	115	75	75-90	—	—	—
Ammonium (acid) <sup>b</sup>	45	54	—	77	84	89	93	78 (dec.)
Potassium (acid) <sup>c</sup>	—	80-140	—	80-150	95-160	100-160	100-160	95
Lithium	—	—	—	229.2- 229.8	223.6- 224.2	224-225	220.5- 221.5	—
Barium	238-239	—	—	> 260	—	dec.	—	100 (dec.)
Calcium	—	—	216	182-183	—	153-156	150-154	83-84
Magnesium	—	—	—	150.4	131.6	121-122	132	—
Thallium <sup>d</sup>	—	—	—	125-126	120-123	115-117	119	83
Lead <sup>e</sup>	85	100	95-100	104.6- 104.8	108.6- 108.8	112.2- 112.4	115.6- 115.8	$\approx 50$
Silver	—	—	—	211-213	211	209	205	—
Mercury (ic)	106.5	—	—	100	—	105	112.2	102-103
Zinc	131-132	135-136	131-132	128	—	129	130	70
Copper (ic)	—	264-266	260	111-113	—	115-120	125	100
Nickel (ic)	—	—	—	44	—	80	80-86	18-20
Cobalt (ic)	—	—	—	—	—	70-75	73-75	—

<sup>a</sup> Valerate,  $108^{\circ}\text{C}.$ ; caproate,  $108^{\circ}\text{C}.$

<sup>b</sup> Caprate,  $68^{\circ}\text{C}.$ ; undecylate,  $72^{\circ}\text{C}.$ ; tridecanoate,  $81^{\circ}\text{C}.$ ; pentadecanoate,  $86^{\circ}\text{C}.$ ; margarate,  $91^{\circ}\text{C}.$

<sup>c</sup> Butyrate,  $85-104^{\circ}\text{C}.$ ; valerate,  $55-120^{\circ}\text{C}.$

<sup>d</sup> Valerate,  $145-147^{\circ}\text{C}.$

<sup>e</sup> Caproate,  $95^{\circ}\text{C}.$ ; caprate,  $103-104^{\circ}\text{C}.$ ; undecylate,  $90-92^{\circ}\text{C}.$ ; hydnoate,  $77-78^{\circ}\text{C}.$ ; chaulmoograte,  $83^{\circ}\text{C}.$

group and of hydrocarbon chains, the unsaturated acids undergo reactions of the double bond.

### SALT FORMATION

The simplest reaction of the fatty acids is the formation of salts on treatment with bases or base-exchange salts. Economically, the most important salts of the fatty acids are those formed with alkali, the alkaline earth metals, and ammonia. The sodium and potassium salts of the higher acids, which are soluble in water, are usually called soaps; they are widely employed, especially the sodium salts, as detergents and as wetting and emulsifying agents (see *Soap*). Other metal salts, which except for the lithium salts are insoluble in water, are usually called metallic soaps. So-called acid salts,  $\text{RCOOM} \cdot \text{RCOOH}$ , formed by sodium, potassium, and ammonium, are actually equimolar mixtures of normal or neutral soaps and free acid. Basic salts as well as normal salts of aluminum, beryllium, lead, and some other metals are on the market, for example,  $\text{Al}(\text{OH})(\text{RCOO})_2$ . The many commercial metallic soaps, which have found important applications for a long time, are not pure compounds. Aluminum, calcium, sodium, lithium, barium, and other salts are important constituents of greases; lead, manganese, cobalt, and other heavy-metal salts of the unsaturated acids are used extensively as driers in the protective-coating industry; sodium, calcium, tin, lead, zinc, and other metallic salts are used as catalysts for various chemical reactions; and zinc, magnesium, and other metallic soaps are used in the preparation of pharmaceuticals and cosmetics. (See *Driers and metallic soaps*.) Although fatty acid salts have been long known, few data are available on the pure compounds. The melting points reported for a number of normal and acid salts of the fatty acids are given in Table XIX (see pp. 887-909 of ref. 7). For the use of salts in the separation of fatty acid mixtures, see page 229.

### ESTERIFICATION

The reaction of fatty acids or their derivatives (acid anhydrides, acid chlorides, or nitriles) with alcohols or phenols leads to esters (see *Esterification*; see also *Ester interchange*):



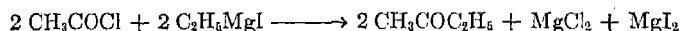
Since the reaction is reversible, esters on hydrolysis yield acids and alcohols or phenols; with the esters of higher molecular weight, elevated temperatures and the presence of an alkali or catalyst are required for rapid reaction. See *Esters, organic*, including Table I, which gives physical constants for some lower esters of saturated fatty acids and oleic and elaidic acids.

Esterification reactions and the products of esterification, whether prepared artificially or found in nature, are of foremost importance in the chemistry of the fatty acids. All vegetable and animal fats and waxes are esters of mono- or polyhydric alcohols; the fats are esters of glycerol and are called glycerides (see *Fats and fatty oils*), while the waxes (*q.v.*) are esters of certain higher monohydric alcohols and higher acids. Also, many esters of complex alcohols and fatty acids, for example, vitamin A palmitate, sterol esters, and sapogenic esters, are known to occur in nature. Since these and other types of esters are found throughout the plant and animal kingdom, esterification may be considered one of the fundamental vital processes.

Many of the fatty acid esters of monohydric alcohols are relatively stable toward heat in the absence of moisture and are therefore generally distillable without decomposition. Hence they are often employed in processes of separation and identification of mixed fatty acids (see p. 230).

### ALKYLATION AND ALKOXYLATION

Alkylating agents such as dimethyl and diethyl sulfates, alkyl halides, metal alkyls or metal alkyl halides, and diazomethane can be used to prepare derivatives of fatty acids, including esters, ethers (of hydroxy acids), ketones, and products with extended normal hydrocarbon chains or branched chains. Thus, ketones of low molecular weight can be prepared by the reaction of acid chlorides with zinc alkyls or magnesium alkyl halides, for example:

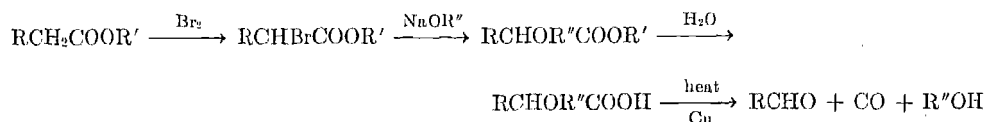


Long-chain symmetrical and unsymmetrical ketones are produced by a modification of the Robinson-Robinson synthesis, which involves the introduction of an alkyl halide and an acid halide into ethyl



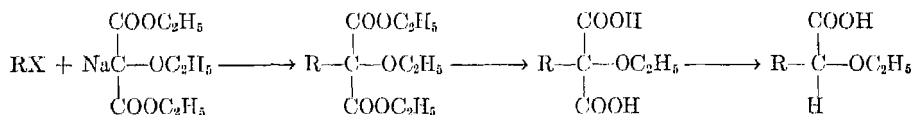
acetoacetate. For example, 12-nonacosanone,  $\text{CH}_3(\text{CH}_2)_{10}\text{CO}(\text{CH}_2)_{10}\text{CH}_3$ , can be synthesized by means of *n*-hexadecyl iodide (prepared from ethyl palmitate by reduction to hexadecanol and iodination) and dodecanoyl (lauroyl) chloride (111). Special methods are available for the preparation of branched-chain fatty acids (see p. 265).

Alkoxylation has been employed to prepare a number of derivatives of the higher fatty acids, for example,  $\alpha$ -alkoxy fatty acids by treating the esters of  $\alpha$ -bromo acids with various sodium alcoholates. The  $\alpha$ -alkoxy fatty acid on heating in the presence of copper undergoes decomposition to the next lower aldehyde, carbon monoxide, and alcohol, according to the following equations (97):



Thus,  $\alpha$ -methoxyheptanoic acid,  $b_p$  122°C., forms hexanal in 70% yield.  $\alpha$ -Methoxylauric acid, m.p. 52°C.,  $b_p$  145°C., similarly prepared, forms undecanal in 75% yield.  $\alpha$ -Methoxystearic acid, m.p. 62.5°C.,  $b_p$  190°C., by heating for 30 minutes at 300°C., decomposes with a theoretical yield of heptadecanal.

$\alpha$ -Ethoxy saturated and unsaturated acids can also be prepared by a form of malonic ester synthesis from the sodium derivative of ethoxymalonic ester by alkylation, hydrolysis of the ester, and decarboxylation of the dibasic acid formed (110).



The  $\alpha$ -ethoxy acid on further heating at 280–300°C. at atmospheric pressure produces the corresponding aldehyde.

## PYROLYSIS

*Decarboxylation of Saturated Acids.* The preparation of ketones (*q.v.*) by heating the calcium or barium salts of fatty acids is a well-known decarboxylation and condensation reaction. Dry distillation of the salts under diminished pressure is generally used in the case of the longer-chain acids. Thus laurone, myristone, palmitone, and stearone have been produced from salts of the corresponding acids. The fatty acids themselves can be pyrolyzed in the vapor state in the presence of various contact substances, such as zinc oxide, thoria, or other oxides; acids of low molecular weight undergo ketonization, whereas higher acids generally undergo cracking, with low yields of ketones (p. 320 of ref. 6). However, when stearic acid is heated 4 hours or more in iron reaction vessels on a commercial scale, stearone is obtained in yields of 91% to practically quantitative.

An aldehyde instead of a ketone is obtained by heating a mixture of calcium formate with a salt of another acid. If the second salt is one of a higher acid such as lauric, myristic, palmitic, or stearic, the product is a dimeric aldehyde,  $(\text{RCHO})_2$ , which can be depolymerized by vacuum distillation.

Still another type of product, one or more hydrocarbons, results when a calcium salt is heated with lime or a metal hydroxide.

*Pyrolytic Decomposition of Unsaturated Acids.* Dry distillation of the alkaline earth salts of unsaturated acids leads to more complex reactions than ketone formation alone. Heating barium oleate produces only a very small amount (2%) of oleone. Sodium oleate pyrolyzed in a vacuum produces principally olefinic hydrocarbons. Vacuum pyrolysis of calcium oleate produces a mixture of oleone, hydroxyoleone, hydroxystearic, and oleic acids. Oleic, elaidic, erucic, and brassidic acids when heated with iron filings give small yields of the corresponding unsaturated ketones.

Considerable work on the pyrolysis of fatty oils and the soaps of their fatty acids has been carried out, in China and Japan as well as other countries lacking natural deposits of petroleum, for the production of hydrocarbons to serve as lubricating oils and fuel oils of the diesel type. Among the products that have been submitted to pyrolysis are the sodium soaps of herring oil, the calcium and magnesium soaps of soybean oil, the calcium soaps of tung oil, and the calcium soaps of peanut oil.

## POLYMERIZATION OF FATTY ACIDS AND MONOESTERS

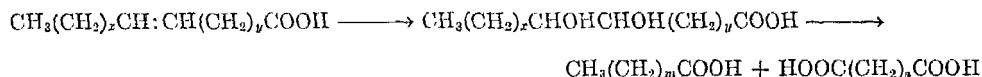
Heat polymerization of fatty oils to produce bodied oils has been practiced for many years (see *Drying oils*), whereas heat polymerization of fatty acids and their monoesters is of very recent practice. Interest was stimulated to a considerable extent by the development of the "theory of functionality" as applied to film formation, production of synthetic resins, oil bodying, and related phenomena. According to this theory, a minimum number of functional groups in the reacting substance are required before polymer formation can occur. In the case of the fatty acids, the functional groups may be unsaturated linkages, hydroxyl groups, and carboxyl groups, two or more of which must be present for heat-polymerization reactions. Thus, the unsubstituted saturated acids are incapable of undergoing heat polymerization *per se*. On the other hand, with compounds containing only double bonds, *addition polymerizations* are possible, and if only hydroxyl and carboxyl groups are present, *condensation reactions* are possible. When both types of functional groups are present, both types of polymerization can occur.

When certain types of polyunsaturated fatty acids are heated under conditions that result in polymerization, the unsaturation decreases through a Diels-Alder mechanism with the formation of essentially dimeric products by the process of ring closure. For example, when the conjugated eleostearic acid or its esters are heat-polymerized, a diene reaction produces a substituted six-membered hydroaromatic ring system.

With nonconjugated fatty acids such as linoleic and linolenic, however, heat polymerization cannot occur through a diene mechanism unless a shift of isolated to conjugated double bonds has taken place. Experiments have reasonably firmly established the fact that isomeric polyene esters, both conjugated and nonconjugated, yield entirely analogous (isomeric) and possibly identical dimers. It has been postulated that the conjugated and nonconjugated methyl octadecatrienoates polymerize by a bimolecular addition, which is followed by, or which also involves, an additional intermolecular ring closure.

## OXIDATION AND HYDROXYLATION

As would be expected, the saturated fatty acids are oxidized only by vigorous oxidizing conditions *in vitro* or by the aid of enzymes *in vivo* (see p. 215), whereas the unsaturated acids (and also hydroxy acids or other partially oxidized acids) are affected by a large number of oxidizing agents, including air at ordinary temperatures (see p. 214) (see also *Oxidation-reduction*). The susceptibility of fatty acids to oxidation is greater the greater their degree of unsaturation (104). Although the oxidation products of unsaturated fatty acids vary with the oxidizing agent and the conditions of oxidation, in general, the first products are hydroxy acids or other oxygen-containing derivatives in which the aliphatic chain remains intact, and subsequent products are mixtures of mono- and dicarboxylic acids (or in some cases aldehydes or aldehydo acids), resulting from cleavage of the chain at the double bond. Thus a simple example of disruptive oxidation would be:



(*m* and *n* may or may not be equal to *x* and *y*, respectively.) With acids containing more than one double bond, each such bond is finally cleaved. However, in many cases, secondary oxidative reactions may occur, or there may be a shift in the position of a double bond. Furthermore, under some conditions inversion of stereoisomers may occur.

**Oxidation by Reagents Other than Atmospheric Oxygen.** Oxidative cleavage has been used in determining the position of double bonds in unsaturated acids but is not always reliable because of variation in the products under different conditions. The same type of reaction serves for the synthesis of certain dicarboxylic acids (see "Oxidation with nitric acid"). Oxidation has been employed in the quantitative analysis of fats and fatty acids (see p. 230).

Where monoethenoid acids are subjected to oxidation, simple distillation serves to separate the two reaction products (mono- and dibasic acids), or they may be partially separated by extraction with ethyl ether and then re-extracted with petroleum naphtha (see also "Oleic acid"). However, with the more complex reaction mixtures resulting from the oxidation of polyethenoid acids or esters, other procedures are sometimes necessary or preferable. Many of the products of oxidation of unsaturated acids have been tabulated by Markley (see pp. 432-38 of ref. 6).



In nonaqueous (acetone) or acidic permanganate solutions, fission of ethylenic acids takes place by direct oxidation, and, theoretically, monoethylenic acids should produce two short-chain acids, one monobasic and the other dibasic. For example, disruptive oxidation of oleic acid should produce only pelargonic and azelaic acids. Although these two acids are generally observed in the products of disruptive oxidation, various other products have also been detected, and the two acids are generally not produced in the same proportions. The explanation lies in the fact that intermediate products of oxidation, such as hydroxy acids, are formed before fission and the fission products are themselves subject to further oxidation. The monobasic acid (pelargonic) oxidizes much more rapidly than the dibasic acid (azelaic), so that appreciably lower yields of the former as compared with the latter acid often result.

Fission may also occur even in the case of alkaline permanganate oxidation by further oxidation of the hydroxy acids first formed, to yield a series of acids containing one less carbon atom than that corresponding to the theoretical fission products. For example, suberic,  $\text{HOOC}(\text{CH}_2)_6\text{COOH}$ , oxalic, and caprylic acids have been obtained from oleic acid by this method.

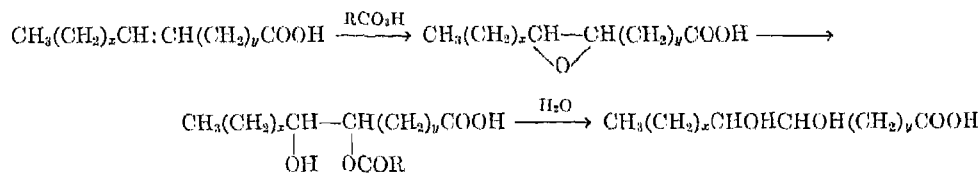
The acetone permanganate method of oxidation has been applied with more success to determining the constitution of polyethenoid fatty acids than has the aqueous alkaline permanganate method. Linoleic acid, when oxidized in acetone solution in the presence of sodium bicarbonate, has been shown to undergo fission at both double bonds to give azelaic, caproic, and oxalic acids, and carbon dioxide.

*Oxidation with Hydrogen Peroxide and Peracids.* The saturated fatty acids are relatively resistant to the action of hydrogen peroxide except in the presence of a catalyst. Most of the fatty acids from acetic to stearic have been subjected to oxidation with hydrogen peroxide in the presence of a catalyst (copper, ammonium salts, alkali phosphates, etc.). Oxidation seldom proceeds as far as carbon dioxide, and a wide variety of partial oxidation products have been identified, including aldehydes, hydroxy acids, ketones, and in the case of the higher acids, acetic acid.

In neutral, weakly alkaline, and weakly acidic solutions, hydrogen peroxide is not generally an effective oxidizing agent even for unsaturated fatty acids. In concentrated acid solutions, with or without an oxidation catalyst, hydrogen peroxide appears to act as a hydroxylating agent. Under alkaline conditions or in the presence of a catalyst, for example copper sulfate, hydrogen peroxide produces mixtures of keto, hydroxy, and dibasic acids, as well as carbonic, formic, and acetic acids from higher monoethenoid acids.

Both inorganic and organic peracids, such as monopersulfuric (Caro's) acid,  $\text{H}_2\text{SO}_5$ , peracetic acid,  $\text{CH}_3\text{CO}(\text{O}_2)\text{H}$ , and perbenzoic acid,  $\text{C}_6\text{H}_5\text{CO}(\text{O}_2)\text{H}$ , have proved useful oxidizing agents for unsaturated fatty acids (see also *Peroxides and peroxy compounds*). The known reaction products resulting from the oxidation of monoethenoid acids include epoxy (oxido) acids, peroxido acids, hydroxy keto acids, and dihydroxy acids. Complete fission appears to occur with monoethenoid acids only as a result of severe hydrolysis of the intermediate oxidation products. Various mechanisms have been proposed for the reaction of peracids with unsaturated fatty acids.

Recent work of Swern and co-workers (102,117,119) indicates that hydroxylation of monounsaturated fatty acids with peracids occurs first through the formation of an epoxy derivative, followed by rupture of the oxirane ring in acid solution with formation of a hydroxy acyloxy derivative, which can be readily hydrolyzed to the corresponding dihydroxy acid:

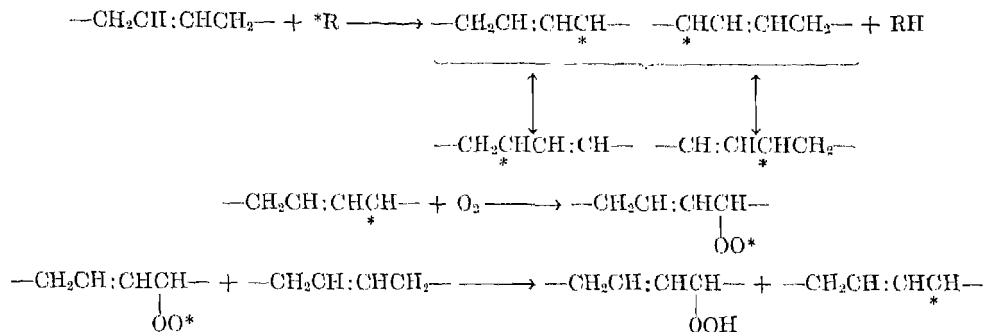


If peracetic acid is used, the epoxy derivative can be isolated in good yield, but, if a small proportion of sulfuric acid is added or performic acid is substituted for the peracetic acid, an almost quantitative yield of the hydroxy acyloxy compound is obtained. Schematic representations of the stereochemical relationships of the various epoxy and dihydroxy oxidation products of the higher monounsaturated fatty acids have been suggested by King (107), Atherton and Hilditch (91), and Swern (116), but some doubt exists as to their validity because the stereochemical interrelationships of all of the products have not been determined.

*Oxidation with Ozone.* Ozone has been used since about 1900 as an oxidizing agent in determin-



bond in an  $\alpha$ -methylene group adjacent to a double bond, leaving an olefinic free radical. Since resonance may be expected to exist between the two forms, the addition of oxygen could take place on either one of the carbon atoms adjacent to the original double bond, or on either carbon atom adjacent to the double bond in the new position:



Farmer concluded that the first isolatable product of autoxidation of methyl oleate (methyl 9-octadecenoate) would be a mixture of 9- and 10-, as well as 8- and 11-hydroperoxides:



This hypothesis received support and substantiation from many sources. Farmer and his co-workers and later other workers isolated the mixed hydroperoxides of methyl oleate (91,100,113,121). Further oxidation of the hydroperoxides or reduction followed by oxidation led to the monosubstituted or fission products that would be expected if hydroperoxide formation takes place in the methylene group adjacent to the double bond of the resonating forms.

The most reactive methylene groups would be those attached to two doubly bonded carbon atoms, as in linoleic acid (9,12-octadecadienoic acid—see p. 274). A shift in position in either one of the double bonds could therefore produce conjugated unsaturation (98,99,101). With compounds containing three or more double bonds, such as linolenic acid (9,12,15-octadecatrienoic acid—see p. 277), the possibilities of isomerism and conjugation among the products are even greater.

It is believed by some that conjugated compounds, instead of forming hydroperoxides, add oxygen at the double bonds to yield peroxides (118).

The mechanism of the next stage after the formation of hydroperoxides or peroxides is still unknown. However, Swift and co-workers have isolated a series of saturated and unsaturated aldehydes from autoxidized fatty acids and fatty oils, which may arise as decomposition products of the hydroperoxides or peroxides (cleavage), and in many fats and oils may be the cause of rancidity (120,122). From hydroperoxidoleates and oleic acid they obtained epoxy and dihydroxy derivatives.

Although there is little doubt that the actual air-drying process (cross linking) is preceded by the formation of hydroperoxides or peroxides, there is less certainty as to the actual details of this reaction itself. It is probable that light catalyzes the cleavage of the O—O bond in the hydroperoxide giving rise to a radical, which can then add to a double bond of another molecule of fatty acid. This adduct radical may then form additional hydroperoxides. The thermal drying process may involve Diels-Alder reactions of conjugated double bonds in one fatty acid molecule with a double bond of another molecule. It is conceivable that some cross linking due to the decomposition of hydroperoxides may also contribute to the thermal-drying process (123a).

**Biological Oxidation.** Although various mechanisms have been proposed for the oxidation of fats in the living organism, it is generally assumed in the case of animals that the fat is first hydrolyzed by lipolytic enzymes to produce glycerol and free fatty acids, and that each constituent is then oxidized (95).

Among the hypotheses that have been proposed to explain the oxidation of fatty acids are those

involving oxidation first at the  $\beta$ -carbon atom ( $\beta$ -oxidation) with fission giving two-carbon fragments, which according to recent work may recombine (109,124); oxidation at the terminal carbon atom ( $\omega$ -oxidation) to dicarboxylic acids, followed in some cases by  $\beta$ -oxidation (123); and simultaneous oxidation at alternate carbon atoms in long-chain fatty acids (multiple oxidation), followed by fission chiefly to four-carbon fragments (105). Acetone, acetoacetic acid, and  $\beta$ -hydroxybutyric acid (called collectively "acetone bodies" or "ketone bodies") have been found in the urine in pathological conditions and are therefore believed to be products of incomplete oxidation.

It has also been suggested that saturated acids are converted into unsaturated acids in the body before oxidation occurs, but this is disclaimed by investigators who find indications of diseased conditions resulting from a diet deficient in unsaturated acids (96).

### HYDROGENATION

Hydrogenation involving addition of hydrogen to double bonds in the aliphatic chain is of paramount importance in the chemistry of fats and oils, but is applied on a more limited scale to fatty acids (see *Fats and fatty oils*). Hydrogenation of fatty acids may involve addition of hydrogen at the C=O group of the carboxyl group to yield alcohols; fatty oils and alkyl esters of the fatty acids may be used as well as the acids themselves. The carbonyl group of keto acids may also be reduced to give unsubstituted acids.

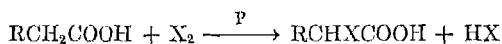
Molecular hydrogen in the presence of a suitable catalyst is generally used industrially. For the saturation of double bonds of fatty acids and esters, nickel catalyst and relatively low temperatures and pressures are generally used; for reduction of the C=O group in the carboxyl group, copper chromite catalyst and moderately high temperatures and pressures are employed. Copper chromite is an effective catalyst also for the reduction of esters (see Vol. 5, p. 835). Modifications of the Bouveault-Blanc sodium-alcohol process are also used industrially for the reduction of esters to alcohols (see *Alcohols, higher*). A similar method is used for reducing nitriles. (See also "Synthesis.")

The Clemmensen and Wolff-Kishner reduction methods have been applied to the reduction of aliphatic keto acids to unsubstituted acids. The former reduction is carried out with zinc amalgam and hydrochloric acid, and the latter with sodium ethoxide and hydrazine hydrochloride. Since the double bond is unaffected by the latter method, it is especially useful for the reduction of unsaturated keto acids (106). Lithium aluminum hydride is another selective catalyst that may be used for the reduction of unsaturated hydroxy, keto, and amino acids, leaving the double bond intact (see Vol. 1, p. 639).

### HALOGENATION

Halogen derivatives of fatty acids, which can be obtained by substitution in saturated acids or by addition to unsaturated acids, are useful in synthesis, purification, analysis, and structure determination because of their ease of formation and their reactivity. In general, the halogen can be removed by reduction to give saturated or unsaturated acids; it can be removed as hydrogen halide (as by aqueous or alcoholic alkali hydroxide) to yield unsaturated acids; or it can be replaced by a hydroxyl or amino group. Reactions of dehydrohalogenation and substitution can take place simultaneously, with a resulting mixture of products (pp. 452-59 of ref. 7). (See also *Halogenation*.)

*Substitution.* Anhydrous saturated fatty acids react with dry chlorine or bromine in the presence of a catalyst such as phosphorus to yield first  $\alpha$ -chloro and  $\alpha$ -bromo derivatives:

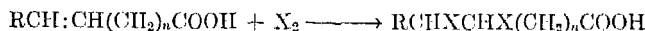


The greater reactivity of the hydrogen atoms adjacent to a carboxyl group is attributed to the activating influence of the double bond in the C=O group. The  $\alpha$ -halogenation of acid chlorides and of esters takes place more readily than in the case of the free acids, but the chlorination of esters is not a simple reaction (103).  $\alpha$ -Iodo acids, which cannot be obtained by direct iodination of the acids, can be prepared from the  $\alpha$ -bromo acids by reaction with potassium iodide.

All of the  $\alpha$ -chloro and  $\alpha$ -bromo acids from acetic to stearic have been prepared by direct halogenation. The higher  $\alpha$ -monobromo acids are soluble in the usual fat solvents and are readily esterified with ethyl alcohol. When refluxed with alcoholic alkalies they are converted into the corresponding  $\alpha$ -monohydroxy acids, which are also soluble in ether, benzene, chloroform, hot ethyl alcohol, and acetic acid.

*Addition of Halogens.* The free halogens chlorine, bromine, and iodine, as well as iodine mono-

bromide and iodine monochloride, generally add to the double bonds of unsaturated acids to form di-halogen derivatives of the corresponding saturated acids:

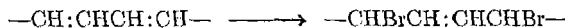


This reaction is the basis of the most widely used constant in analytical work on fats and fatty acids, the iodine value (I.V.); furthermore, bromo derivatives have served for the separation of mixtures of unsaturated acids (see p. 230). Relatively little addition of halogen occurs at a double bond in the proximity of the carboxyl group, whereas relatively complete addition occurs at remote double bonds, whether located near the center of a long aliphatic chain or at a terminal methylene group. Even when the reaction time is extended to 70 or more hours, the addition of halogen to 2-octadecenoic acid is only about 50% of the theoretical. The effect of increasing distance of the double bond from the carboxyl group is illustrated by the iodine values of 2-, 3-, and 4-octadecenoic acids by the Hübl method, which were found to be 9.04, 16.27, and 29.96, respectively, compared with 89.87 required by theory. Ordinary oleic acid (the 9,10-isomer), however, exhibits the theoretical iodine value.

If the concentration of halogen, reaction temperature, or reaction time is excessive, some substitution in the hydrocarbon chain occurs. Therefore, both in the quantitative determination of unsaturation and in the preparation of derivatives, these conditions must be rigidly controlled. In the quantitative determination of unsaturation, dilute solutions of the halogenating agent are used at room temperature for a specified time. For the preparation of derivatives, for example, bromo addition products, the halogen is added very slowly at low temperatures, 0 to  $-10^\circ\text{C}$ . The rate of reaction is also affected by light of various wave lengths and catalysts, such as mercuric chloride and mercuric acetate.

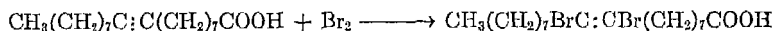
The naturally occurring monoethenoid acids generally add halogens normally to produce di-halogenated derivatives. The lower members of the series are liquids at room temperature. In the case of positionally isomeric halogen derivatives of long-chain monoethenoid acids, the melting point decreases as the distance of the halogen from the carboxyl group increases. In the case of the stereoisomeric halogen derivatives of cis-trans isomeric acids, the derivatives of the trans isomers melt above those of the corresponding cis isomers, as do the acids; the difference, however, is small between the two 9,10-dibromostearic acids (m.p. 29-30 and  $28.5-29^\circ\text{C}$ .) from elaidic (trans) and oleic (cis) acids, respectively.

Most polyunsaturated acids having all of their double bonds in nonconjugated position add halogen normally, one mole of halogen per double bond, apparently in stepwise fashion, with the production of a mixture of stereoisomers (pp. 336-37 of ref. 6). On the other hand, if the double bonds are conjugated, halogen addition, when carried out by methods normally employed with nonconjugated acids, is generally erratic and incomplete. Whereas normal linoleic (9,12-octadecadienoic) acid adds two moles of halogen, 9,11-octadecadienoic acid adds one mole of halogen normally, but the second mole only slowly and incompletely even after many hours. This behavior is very suggestive of the 1,4-addition observed with many dienes, with the simultaneous formation of a new double bond at the 2,3-position:



In the case of doubly conjugated acids, for example, eleostearic acid, halogen adds normally to two of the three double bonds but with considerable difficulty, or not at all, to the third double bond. It is not unlikely that 1,4-addition may occur with either pair of conjugated double bonds with formation of a new double bond, which does not add halogen, whereas the remaining original double bond would be reactive. It has been observed that in the presence of some agents, like mercuric acetate, halogens can be made to add quantitatively or very nearly so to conjugated double bonds.

Stearolic, behenolic, and similar acids containing a triple bond add only one molecule of halogen, as for example:

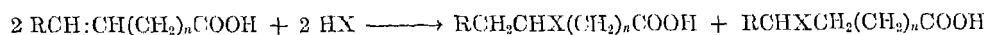


Similarly, 10-undecynoic acid,  $CH_3C(CH_2)_8COOH$ , adds only one mole of halogen by the Hanus iodine method.

*Addition of Hydrogen Halides (Hydrohalogenation).* Hydrogen halides,  $HX$ , add to the double bonds of monounsaturated fatty acids under certain conditions to form monohalogen derivatives of the corresponding saturated acids. The hydrogen halides are considerably less reactive in this respect than are the halogens themselves or the oxygenated halogen acids,  $HOX$ , and their reactions may therefore be more readily controlled.



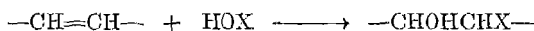
As in the case of other unsymmetrical compounds containing a double bond, two isomeric monohalogen derivatives may be formed by addition of hydrogen halides:



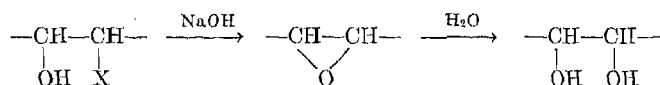
The relative amounts of the two products depend upon several factors, such as the electronic structure of the acids (in particular the apparent polarity of the double bond as influenced by its distance from the carboxyl group and the nature of the groups attached to it), the conditions used (notably the presence or absence of oxygen or peroxides and the use of a solvent), and to some extent the nature of the hydrogen halide.

The addition of hydrogen halides to undecenoic acids was studied by Smith and co-workers (89,90). In any solvent and in the absence of air, addition of hydrogen bromide to 10-undecenoic acid,  $\text{CH}_2\text{:CH}(\text{CH}_2)_8\text{COOH}$ , produces primarily 10-bromoundecanoic acid,  $\text{CH}_3\text{CHBr}(\text{CH}_2)_8\text{COOH}$ , m.p.  $35.1^\circ\text{C}$ ., in accordance with the Markovnikov rule of halogen addition. In the presence of air the reaction product will vary with the solvent, some solvents enhancing and some hindering the so-called peroxide effect; in petroleum naphtha solution, for example, 11-bromoundecanoic acid,  $\text{CH}_2\text{BrCH}_2(\text{CH}_2)_8\text{COOH}$ , m.p.  $51^\circ\text{C}$ ., is the principal product. The addition of hydrogen bromide to ethyl 10-undecenoate is entirely analogous to the addition to the free acid. However, the addition of hydrogen chloride or hydrogen iodide to 10-undecenoic acid under either oxidizing or nonoxidizing conditions yields mainly 10-chloroundecanoic acid, m.p.  $32^\circ\text{C}$ ., or 10-iodoundecanoic acid, m.p.  $22\text{--}23^\circ\text{C}$ . (89). The isomeric 9-undecenoic acid,  $\text{CH}_3\text{CH:CH}(\text{CH}_2)_7\text{COOH}$ , whose double bond is not in the terminal position, adds hydrogen bromide to give equal amounts of 9- and 10-bromoundecanoic acids. The equilibrium ratio of these two isomers is unaffected by the presence of catalysts or solvent, but the rate of reaction is affected by the solvent used.

*Addition of Hypohalous Acids.* Hypochlorous acid and its bromine and iodine analogs add directly to the double bonds of unsaturated fatty acids to form halohydrins.

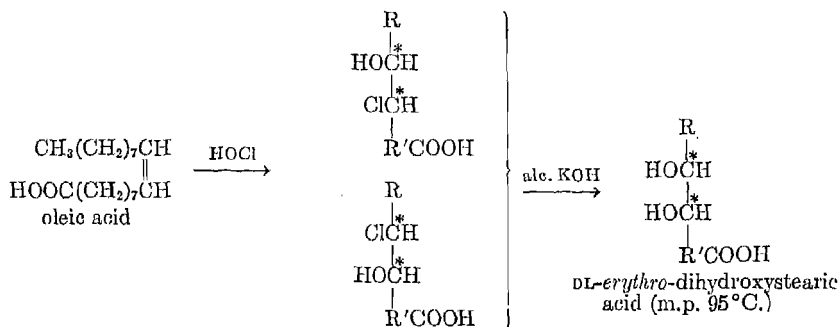


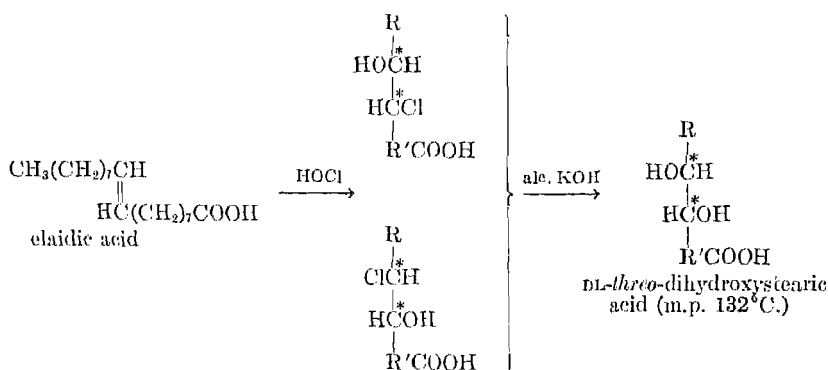
Such reactions resemble hydrohalogenations because the hypohalous acid apparently functions as  $\text{HO-X}^+$ , and the direction of addition to an ethylenic bond is subject to the same considerations as additions involving hydrogen halides. Like other halohydrins (see *Chlorohydrins*), these on treatment with aqueous or alcoholic alkalis are converted to epoxides and dihydroxy derivatives:



Except as intermediates for the preparation of the polyhydroxy acids, the halohydrins derived from fatty acids have been of no great practical value. Most of the investigators of the addition products of the higher unsaturated acids with hypochlorous and hypobromous acids have been concerned with problems of position isomerism and stereoisomerism.

The hydroxyl group and halogen atom of hypochlorous acid can add to oleic acid, for example, at either the ninth or tenth carbon atom to yield a mixture of racemic 9-hydroxy-10-chloro- and 9-chloro-10-hydroxystearic acids. Elaidic acid similarly gives two racemic chlorohydroxystearic acids. Each pair of addition products on hydrolysis yields a dihydroxy acid, also containing two asymmetric carbon atoms, indicated by asterisks in the following formulas.





Similar studies have been carried out on erucic and brassidic acids.

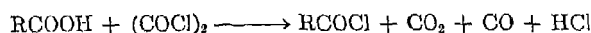
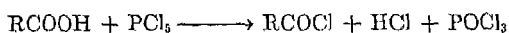
*Preparation of Acid Halides (q.v.).* Although any of the halogens may be substituted for the hydroxyl group of the carboxyl group of fatty acids, only the chlorides of the higher acids have been extensively prepared and used. The acid chlorides are generally liquids at room temperature, and possess a pungent odor and fume in contact with air owing to their ready hydrolysis in contact with water. The boiling points of the acid halides increase as the molecular weights of the halogens increase from fluorine to iodine and as the homologous series is ascended. Alternation does not occur in the melting points as it does in the melting points of the ascending series of acids. See Table XX. For a discussion of the naming of acyl radicals, see page 178.

Bauer reported a comprehensive and systematic investigation of the preparation of the higher fatty acid chlorides by reaction of the acids (lauric, myristic, palmitic, stearic, oleic, elaidic, and linoleic) with phosphorus tri- or pentachloride, thionyl chloride, oxalyl chloride, or phosgene (92).

TABLE XX. Properties of Fatty Acid Chlorides.

I.U.P.A.C. name	Synonyms	Formula	M.p., °C.	B.p., °C.
Acetyl	Ethanoyl	$\text{CH}_3\text{COCl}$	-112	51-52
Propionyl	Propionyl	$\text{C}_2\text{H}_5\text{COCl}$	-94	78-80
Butyryl	Butyryl	$\text{C}_3\text{H}_7\text{COCl}$	-89	101-102
Valeroyl	Valeryl	$\text{C}_4\text{H}_9\text{COCl}$	-110	128
Caproyl	Hexanoyl	$\text{C}_5\text{H}_{11}\text{COCl}$	-87.3	152-153
Heptanoyl	Enanthoyl; enanthyl	$\text{C}_6\text{H}_{13}\text{COCl}$	-83.8	175
Octanoyl	Capryloyl; caprylyl	$\text{C}_7\text{H}_{15}\text{COCl}$	-61	195
Nonanoyl	Pelargonoyl; pelargonyl	$\text{C}_8\text{H}_{17}\text{COCl}$	-60.5	220
Decanoyl	Capryl; caprinoyl	$\text{C}_9\text{H}_{19}\text{COCl}$	-34.5	114 <sub>15</sub>
Undecanoyl	Hendecanoyl	$\text{C}_{10}\text{H}_{21}\text{COCl}$	—	—
Lauroyl	Dodecanoyl	$\text{C}_{11}\text{H}_{23}\text{COCl}$	-17	142 <sub>15</sub>
Myristoyl	Tetradecanoyl	$\text{C}_{13}\text{H}_{27}\text{COCl}$	-1	168 <sub>15</sub>
Palmitoyl	Hexadecanoyl	$\text{C}_{15}\text{H}_{31}\text{COCl}$	12	192 <sub>15</sub>
Stearoyl	Octadecanoyl	$\text{C}_{17}\text{H}_{35}\text{COCl}$	23	215 <sub>15</sub>
10-Undecenoyl	10-Hendecenoyl	$\text{C}_{10}\text{H}_{19}\text{COCl}$	—	128.5 <sub>14</sub>
Oleoyl	cis-9-Octadecenoyl	$\text{C}_{17}\text{H}_{33}\text{COCl}$	—	213 <sub>13</sub>
Elaidoyl	trans-9-Octadecenoyl	$\text{C}_{17}\text{H}_{33}\text{COCl}$	—	216 <sub>13</sub>

He concluded on the basis of yields, ease of handling, and cost of reagent, that phosphorus tri- and pentachlorides are superior to other chlorinating agents for the preparation of pure saturated acid chlorides, and that oxalyl chloride was preferable for use in preparing unsaturated acid chlorides.



Owing to the great lability of the chlorine atom in the acid chlorides, they are very useful intermediates in the synthesis of glycerides, other esters, amides, and ketones. The higher acid chlorides have been used in the preparation of wetting agents and detergents by reaction with, for example, hydroxy-sulfonates or amino sulfonic acids (p. 812 of ref. 7).

#### MISCELLANEOUS DOUBLE-BOND ADDITION REACTIONS

Unsaturated fatty acids have been treated with phosphorus, arsenic, and mercury compounds with the production of a variety of end products; of these, the phosphorus derivatives are most numerous. Phosphorus, phosphorus pentoxide, phosphorus trihalides, and acetylphosphoric acid, arsenic trichloride and potassium arsenate, and mercuric acetate have been used to introduce phosphorus, arsenic, and mercury, respectively, at the double bonds of unsaturated acids. The constitution of most of the reaction products is not known with certainty. The products have been proposed for use as therapeutic agents, herbicides, etc.

The reactions of maleic anhydride with unsaturated fatty acids as well as with drying oils (*q.v.*) have been extensively investigated (93,94,113) (see "Linoleic acid," p. 274; "Linolenic acid," p. 277; *Maleic acid and maleic anhydride*).

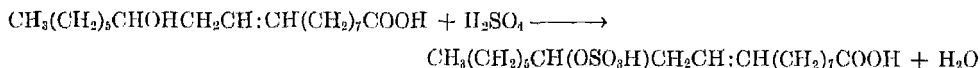
#### REACTIONS WITH SULFUR COMPOUNDS

The reagents used in forming sulfur derivatives of fatty acids include elemental sulfur, phosphorus sulfide, sodium hydrosulfide, NaHS, sulfur monochloride, S<sub>2</sub>Cl<sub>2</sub>, thiocyanogen, (SCN)<sub>2</sub> (see p. 229), *S*-benzylthiuronium chloride, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SC(NH<sub>2</sub>):NH<sub>2</sub>Cl, and the various sulfating and sulfonating agents, sulfuric acid, oleum, sulfur trioxide, and chlorosulfonic acid. The most thoroughly investigated classes of these derivatives are the thio acids (*q.v.*), and their esters and the sulfated and sulfonated acids and esters. The higher aliphatic thio acids do not appear to have been prepared, but a number of their alkyl esters have been prepared and their properties tabulated by Ralston, Segebrecht, and Bauer (112).

**Sulfates and Sulfonates.** Although sulfated and sulfonated oils and fatty acids have been known for about a century, the two types of products have often been confused and the commercial products are not usually definite chemical compounds. In sulfates the sulfur is attached to carbon through oxygen (—C—O—S—), whereas in sulfonates the sulfur is linked directly to carbon (—C—S—). The former linkage is relatively easily broken by hydrolysis in comparison with the more stable carbon-sulfur linkage.

**Sulfation Reactions.** The higher saturated fatty acids, for example, palmitic, dissolve in concentrated sulfuric acid without change and can be recovered by dilution with water. On the other hand, the doubly bonded carbon atoms of unsaturated acids readily add sulfuric acid with the formation of the corresponding hydrogen sulfates. This difference in reactivity toward sulfuric acid is used as a means of removing ethylenic impurities in preparing highly pure saturated acids. Addition of sulfuric acid to ethylenic acids at temperatures of 0–15°C. followed by dilution with water and hydrolysis by boiling with water or dilute alkali solutions yields hydroxy acids, ketones, and some secondary reaction products. Acetylenic acids on treatment with sulfuric acid and hydrolysis yield saturated keto acids.

Hydroxy acids when treated with sulfuric acid or chlorosulfonic acid also yield sulfuric esters (hydrogen sulfates). An unsaturated hydroxy acid, such as ricinoleic acid, is esterified by sulfuric acid at 20–35°C., according to the equation:



At –5 to +10°C., sulfation at the double bond of ricinoleic acid takes place. See "Ricinoleic acid" (p. 291); *Castor oil*.

Various oils, fatty acids and their esters, and fatty alcohols are subjected on an industrial scale to the action of sulfuric acid to form important products similar to those obtained from oleic and ricinoleic acids (115). These products were first applied in mordant dyeing of textiles but are now used in a variety of textile operations (see *Surface-active materials*; *Textile chemical specialties*).

Sulfation of fatty oils by means of sulfuric acid may be accompanied by hydrolysis of the glyceride and of the sulfate, followed by other reactions involving formation of lactides and estolides (internal esters) as well as some dimerization. The di- and monoglycerides formed by hydrolysis are,

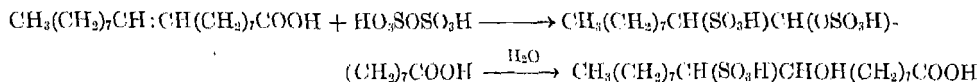
in whole or in part, esterified with sulfuric acid to form heteroglycerides containing both fatty acid and inorganic radicals. Properly controlled sulfation of fats and oils can be carried out with little hydrolysis and good yields of true sulfated products.

During sulfation, unsaturated fatty acids, like the oils, may undergo hydrolysis and other reactions. Tetrameric compounds were isolated from sulfated oleic acid, which were assumed to have been formed by interesterification between the carboxyl and hydroxyl groups of the hydrolyzed sulfated acid. These estolides are not readily hydrolyzed by mineral acids but, on alkaline hydrolysis, apparently regenerate monomeric hydroxy acids. In a patented process, sulfation with sulfuric acid or oleum followed by alkaline hydrolysis gives high yields (70–75%) of hydroxy acids, as compared with yields of 50% or less normally obtained by acid hydrolysis. Evidence has been obtained that the hydroxyl groups in the products of unsaturated fatty acids sulfated under certain conditions are attached to carbon atoms considerably removed from the double bond, but the mechanism of the reaction has not yet been established (see pp. 524–25 of ref. 6).

It is evident, therefore, that the so-called "sulfonated" (actually sulfated) oils, acids, and esters of commerce consist of various mixtures of sulfated oil, sulfated acids, sulfuric acid esters, hydroxy acids, estolides, lactides, and di- or higher polymeric substances, depending on the nature of the raw material and the conditions of "sulfonation" (sulfation).

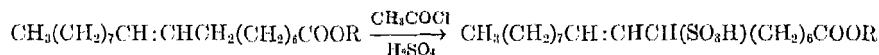
**Sulfonation Reactions.** True sulfonic acids (*q.v.*) may be prepared by a variety of methods but particularly by carrying out the sulfonation in a relatively anhydrous medium. Fuming sulfuric acid (oleum), sulfur trioxide, and chlorosulfonic acid are generally employed in treating unsaturated acids or oils containing these acids for the production of true sulfonated products.

With fuming sulfuric acid and oleic acid, for example:

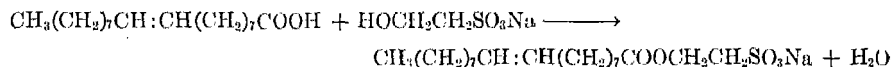


the product probably contains both a sulfate and a sulfonic acid group, which on hydrolysis with water is converted to a hydroxy sulfonic acid.

If the reaction with sulfuric acid is carried out in the presence of an organic acid anhydride or chloride, sulfonation is claimed to occur at a carbon atom adjacent to the double bond. Thus, methyl oleate when treated with acetyl chloride and sulfonated at 0°C. with sulfuric acid is said to produce among other products a sulfonic acid:



In another type of true sulfonates derived from fatty acids, the carbon-sulfur bond is in an ester group. Sodium oleoylethanesulfonate (Igepon AP), for example, may be prepared by esterifying oleic acid or its chloride with sodium isethionate (115):



A similar product, a substituted amide,  $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{CON}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$  (Igepon T), is formed from oleic acid or its chloride and *N*-methyltaurine,  $\text{NH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$  (115).

**Action of Sulfur and Sulfur Monochloride.** The higher saturated fatty acids do not react with sulfur even at moderately elevated temperatures (130°C.), whereas unsaturated acids are readily reactive under the same conditions. The sulfur adds to the double bonds without appreciable evolution of hydrogen sulfide until temperatures of 150–200°C. are reached. Sulfur monochloride reacts vigorously with unsaturated fatty acids to yield products containing both sulfur and chlorine, apparently by simple addition, although substitution also occurs under most conditions.

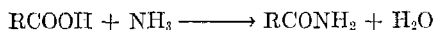
### Nitrogen Derivatives

The commercial production of nitrogen derivatives of fatty acids is based largely on the reactions of the acid with ammonia. Two types of chemicals, the amides and the nitriles, which result from this reaction, are in large-scale production. Fatty acid amines, prepared by the catalytic hydrogenation of the nitriles, are commercially the

most important nitrogen derivatives of the fatty acids. The newest nitrogen-containing derivatives to achieve importance are the quaternary ammonium compounds.

#### FATTY ACID AMIDES

Fatty acid amides (see *Amides*) have the general formula  $RCONH_2$ , and are prepared by treating a fatty acid with ammonia (6,7,137,145), according to the equation:



In practice, fatty acids are placed in a stainless-steel, agitated, pressure vessel and heated to about  $200^\circ\text{C}$ ., at which temperature ammonia is fed into the acids. By-product water and excess ammonia are vented continuously, the water being condensed and the ammonia recirculated through the reactor. A slight pressure is maintained in the apparatus. The reaction is rapid at the onset, but 8-10 hours is required to attain complete conversion of the fatty acid to the amide.

Fatty acid amides are commercially available in over 90% purity from caprylic, capric, lauric, myristic, palmitic, and stearic acids, and also as mixtures from the fatty acids of coconut oil, beef tallow, hydrogenated beef tallow, red oil, soybean oil, and tall oil (127,130). The price is largely dependent on the value of the starting fatty acid, and in 1950 varied from 35¢ to \$1.50 per pound.

The fatty acid amides are waxlike, neutral products varying in melting point from  $55^\circ\text{C}$ . for tall-oil amide to over  $100^\circ\text{C}$ . for stearamide. Physically they range from a soft paste to a hard material, which can be flaked. Fatty amides are insoluble in water, but above their melting points are appreciably soluble in common organic solvents (7,127,130,141).

Chemically the amides are moderately active and undergo most reactions described for short-chain amides (see *Amides*). It is their chemical reactivity, in fact, that makes it possible to convert them to a number of high-melting waxes and wax additives, as well as water repellents and softeners for textiles. Use of the amides as mutual solvents makes possible the blending of waxes with plastics. Other applications in the plastics field would include their use as antitack or antiblock agents. Important, too, are their uses as bloom-prevention compounds in rubber products, ink additives for reducing slip and gloss, and as surface-active agents (127,130).

#### FATTY ACID NITRILES

Fatty acid nitriles (see *Nitriles*) or alkyl cyanides have the general formula  $RCN$ , and are produced commercially by reaction of ammonia with a fatty acid (6,7,135,137,145), according to the equation:



Industrially, conversion of fatty acids to nitriles is carried out as shown in Figure 22 (139,140,147,149,150). The acid, heated to  $240^\circ\text{C}$ ., is introduced onto one of the lower plates of a bubble-cap ammoniation tower, the bottom of which contains a heater maintained at about  $315^\circ\text{C}$ . to vaporize the liquid nitrile and fatty acid collecting there. Bottoms are drawn off the ammoniation tower and passed into the pitch tower where they are swept free of nitrile and unreacted fatty acid by ammonia at  $360^\circ\text{C}$ ., which enters the ammoniation tower by way of the pitch tower. This stream enters the ammoniation tower beneath the surface of the liquid in the vaporizer. The mixed vapors rise through the tower, and by the time they leave the reactor an 80% conver-

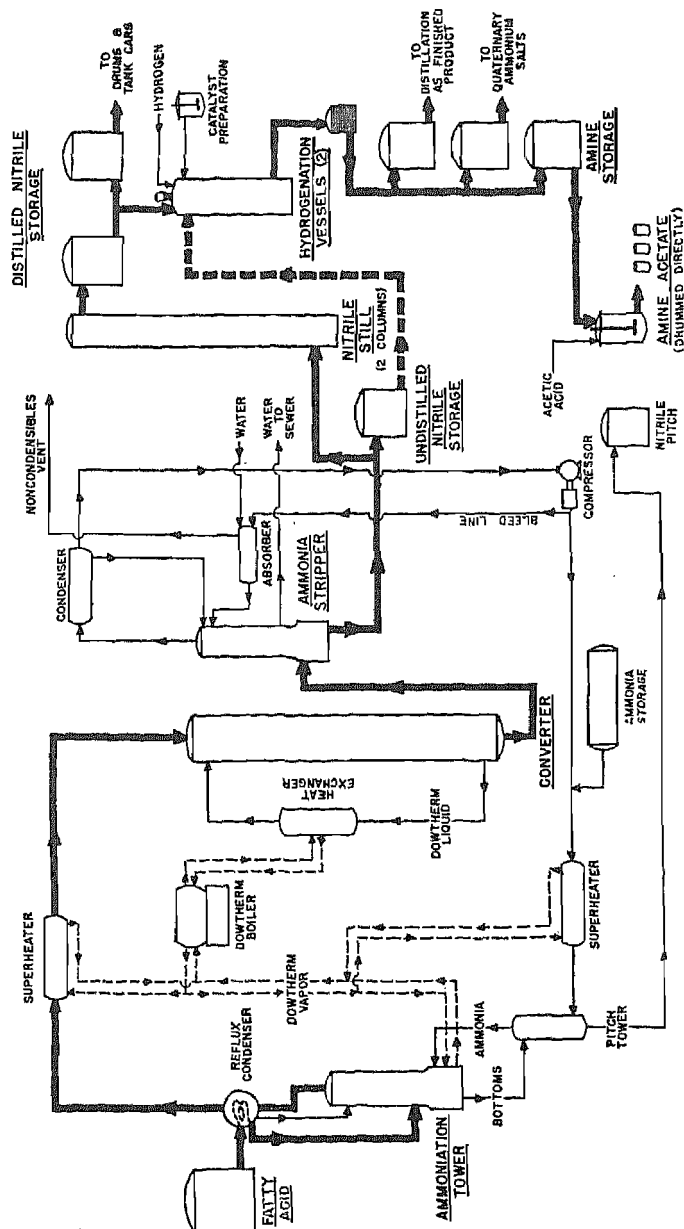


Fig. 22. Nitrile and amine production (137).

sion of fatty acid to nitrile has been effected. About 50% of the vapors, composed of nitrile, fatty acid, ammonia, and water, is condensed and returned to the tower as reflux. The balance, after being subjected to further heating, enters the top of a shell-and-tube converter containing a fixed bed of aluminum oxide catalyst. A temperature of 360°C. is maintained in this unit also, and it is here that the conversion to nitrile is completed. From here the vapors, composed primarily of nitrile with less than 0.5% of water and unreacted fatty acid and ammonia, are passed into a stripping column

where the ammonia and water are removed. The ammonia is condensed and compressed for re-use. The nitrile is delivered to storage or to vacuum-distillation equipment, similar to that used for fractionation (see p. 236). All equipment is of stainless steel up to a point where fatty acid is present in negligible amounts, with the balance of ordinary steel.

Nitriles are commercially available from caprylic, capric, lauric, myristic, palmitic, and stearic acids, as well as overall mixtures of the fatty acids from coconut oil, hydrogenated beef tallow, soybean oil, and tall oil (128,130). The purity, based on nitrile content, is over 99% for the distilled products. The price in 1950 varied from 33¢ to \$1.50 per pound, depending on the fatty acid from which the nitrile was made.

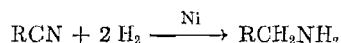
The fatty acid nitriles range from liquids to solids, palmitonitrile, stearonitrile, and hydrogenated-tallow nitrile having melting points above room temperature. The nitriles are insoluble in water, but are very soluble in organic solvents, exhibiting greatest solubility in polar solvents (135).

Chemical reactivity of the nitriles is attributed to the unsaturation, and therefore additions to this unsaturation account for the importance of the nitriles as intermediates for other chemicals (see *Nitriles*). The application of fatty nitriles to specific uses has never approached the same importance as their use as precursors for other derivatives, but their consumption as synthetic-rubber and synthetic-fiber plasticizers, as corrosion inhibitors for steel, and as lubricants in yarn spinning is increasing (128, 130).

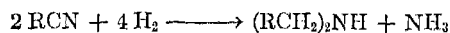
#### FATTY ACID AMINES

The fatty amines can be considered as substituted ammonias, in which one or more hydrogen atoms on the nitrogen have been replaced with the alkyl chain of the fatty acid. Mono-, di-, and trisubstitution can occur, resulting in primary ( $\text{RNH}_2$ ), secondary ( $\text{R}_2\text{NH}$ ), and tertiary ( $\text{R}_3\text{N}$ ) amines (see *Amines*). Of these, only the primary and secondary amines are in large-scale production.

Many methods of preparing amines have been proposed, several of which have been applied industrially. In practice, however, catalytic hydrogenation of the nitrile has found widest acceptance for producing fatty amines (7,133,148). This reaction proceeds according to the equation:



under conditions selected to yield primary amines. Commercially the fatty nitrile is slurried with ½–1% Raney nickel and pumped into a stainless-steel, high-pressure, stirred autoclave. After being heated to about 150°C., the nitrile is blown with hydrogen at 200–250 p.s.i. for about 3–4 hours to complete conversion to the amine. The product leaving the reactor is composed of about 85% primary amine, the balance being composed of secondary amine and minor amounts of tertiary amine (137,139). Primary amine is separated from the impurities by distillation through a pot still and is then pumped to storage under nitrogen to prevent reaction with atmospheric carbon dioxide, which yields the carbamate salt. Secondary amines are prepared in a similar manner, except that higher temperatures (200–250°C.) are employed, and the ammonia that forms as a by-product, according to the following reaction, is continuously removed.



Primary fatty amines are available commercially in distilled and undistilled grades from caprylic, capric, lauric, myristic, palmitic, and stearic acids, and from the mixed acids obtained from coconut oil, soybean oil, tallow, and hydrogenated tallow. The amine prepared from tall-oil fatty acids is also available as the undistilled product (126,130). The purity of the distilled amines, based on amine content, is over 99%, and the price, again based on the value of the starting fatty acid, ranges from 35¢ to \$2.00 per pound. Amines are also available as the acetate salts. These compounds are prepared by continuous neutralization of the amine with acetic acid.

The amines are oily liquids or solids, depending upon chain length and degree of unsaturation, and are essentially insoluble in water but soluble in most organic solvents, both polar and nonpolar (133,142).

Chemically the fatty amines exhibit most of the reactions of the lower-molecular members of the series (see *Amines*). The most characteristic reaction of the fatty amines is that of salt formation, which they display with both inorganic and organic acids. The salts are in general water-soluble, cationic, surface-active materials.

Two secondary fatty amines are available (126), one prepared from the nitrile of coconut-oil fatty acids, m.p. 46°C., and the other from the nitrile of hydrogenated-tallow fatty acids, m.p. 68°C.; both contain over 90% secondary amine. In 1950, coconut-oil amine sold at about 57¢/lb. and hydrogenated-tallow amine at about 43¢/lb.

The secondary amines are insoluble in water but are soluble in most organic solvents (136).

The primary fatty amines provide a convenient starting material for the synthesis of a wide variety of industrial chemicals including synthetic detergents, wetting agents, germicides, and oil additives. Discussion of the uses of amines will be general rather than specific regarding chain length, although in some applications the correct choice of chain length is essential for maximum usefulness.

Utilization of the fatty amines themselves is of significant importance in many fields (126,130,131,132). In the rubber industry, they are useful in the reclaiming of rubber; they act as mold-release agents, extrusion lubricants, and scorch-preventives in the compounding of butyl rubber. The coating industry applies amines as grinding, softening, and dispersing agents for pigments and for improving the adhesion of primer paints to damp or rusty surfaces. Amines also find use as additives in corrosion inhibitors, lubricating oils, slushing compounds, cutting oils, metal cleaners, calking compounds, and asphalt tiles.

The acid salts (primarily the acetate) have found even more extensive industrial utilization than the free amines (125,126,130,131,132). Nonmetallic-ore flotation, both froth flotation and agglomeration, employs amine salts for many separations, such as the isolation of phosphates from silicates, and sylvite (potassium chloride) from halite (sodium chloride). The use of amine salts improves the "hand" and softness of textiles. Application in the metals industry would include their use as emulsifiers for drawing compounds, rust and corrosion inhibitors, surface-active agents for solvent and emulsion degreasers, and as a core-oil additive for improving the coating of foundry sand. The use of fatty amine salts as a means of preventing the accumulation of static charges on plastics, textiles, and printing rollers is increasingly important. The addition of amine salts to primer and asphalt paints enhances their adhesion on damp or corroded surfaces. Similarly, addition to asphalt promotes antistrip action when coated agglomerates are used in road construction. The amine salts, like the



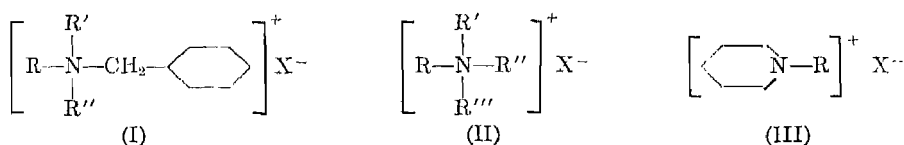
amines, are applied as color-flushing agents, in rubber compounding, in waterproofing cloth and fiberboard, and as germicides, fungicides, and insecticides.

The secondary amines, although available only comparatively recently, have found use in lubricants, as rust inhibitors, as rubber-processing chemicals, textile-treating agents, synthetic waxes, and as chemical intermediates (126).

#### QUATERNARY AMMONIUM COMPOUNDS

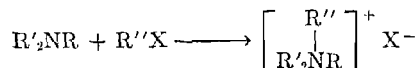
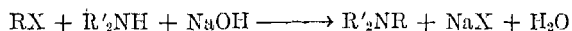
Quaternary ammonium compounds, since about 1940, have attained noteworthy prominence in the fields of flotation and germicides and antiseptics (see *Flotation; Quaternary ammonium compounds*). Continued studies of the properties of these compounds have expanded the many applications in other fields, largely based on their surface-active and wetting properties.

An increasing number of quaternary ammonium salts are being produced commercially, but this discussion is restricted to those in whose manufacture fatty acids serve as a starting material. These can be classified roughly according to the following types: trialkylaralkylammonium halides (I); tetraalkylammonium halides (II); and alkylpyridinium halides (III):

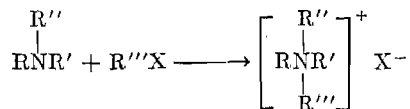


where R is an alkyl radical of 6-18 carbon atoms, either saturated or mono- or di-unsaturated. R', R'', and R''' are usually methyl groups but one or more can be ethyl or higher alkyl groups (138).

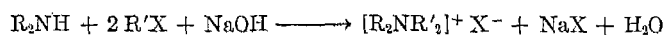
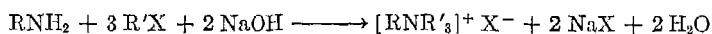
Commercially the quaternary ammonium salts are prepared by two general methods (129,138). In the first, a long-chain alkyl halide (derived from a fatty acid through the alcohol) is treated with a dialkylamine and then with an alkyl or aralkyl halide to yield the quaternary salt:



A variation of this method involves the reaction of the long-chain alkyl halide with a tertiary amine, either alkyl, mixed alkyl-aryl, or heterocyclic, to produce the quaternary ammonium salt directly:



The second method involves the reaction of a fatty primary or secondary amine with an alkyl halide to yield the quaternary ammonium salt:



The commercial production of quaternary ammonium compounds by this second method is carried out by reaction of the primary or secondary amine with an alkyl

halide such as methyl chloride in the presence of water or an organic solvent such as isopropyl alcohol. Sodium hydroxide is added in the theoretical amount necessary to neutralize the by-product acid. This process, which is exhaustive alkylation, is performed in an agitated, stainless-steel, pressure vessel.

Quaternary ammonium salts are usually marketed as aqueous or organic-solvent solutions containing from 10 to 75% of the salt. Since the preparation of these substances is carried out in either an aqueous or solvent medium, and since the pure materials are hygroscopic, it is undesirable and usually unnecessary to isolate them from solution. When the solutions are designed for specific applications, such as germicidal or sanitizing agents, they may also contain other ingredients such as non-ionic surface-active agents. Up to the present time, the quaternary ammonium salt most widely used in germicidal and antiseptic applications is the alkyldimethylbenzylammonium chloride in which the alkyl groups correspond to those derived from coconut-oil fatty acids (138).

Quaternary ammonium salts containing one long-chain alkyl group having 12, 14, 16, or 18 carbon atoms are available, as well as overall mixtures containing the alkyl groups found in coconut-oil fatty acids, tallow fatty acids, and soybean-oil fatty acids. Compounds with two long chains are offered containing the mixed alkyl chains of coconut-oil fatty acids and hydrogenated-tallow fatty acids.

The price of the alkyl quaternary ammonium compounds is dependent upon the type of alkyl chain employed and on the concentration of the active ingredient; in 1950, it varied from 25 to 65¢ per pound.

Chemically, the commercially important quaternary ammonium salts are usually chlorides or bromides. These salts are stable at the temperatures usually encountered in their use. At elevated temperatures (above 100°C.) and atmospheric pressure, an increasing tendency toward decomposition into alkyl halide and tertiary amine is observed. Aqueous solutions of the salts are thermally stable although, in the presence of strong alkali, formation of the much less stable quaternary ammonium hydroxides occurs to some extent.

Physically, the quaternary ammonium salts containing one or more long alkyl chains exhibit the surface-active properties of colloidal electrolytes (138,143,144). The high germicidal activity of these salts is attributed to these properties. Solubility characteristics of the quaternary ammonium salts are dependent upon the type of substitution, those containing a predominance of shorter chains (8–14 carbon atoms) being very soluble in water, whereas those containing longer chains (16 or 18 carbon atoms) are much less so. The salts containing one long alkyl chain are soluble in water and polar organic solvents but are insoluble in nonpolar solvents, whereas those containing two or more long chains are almost insoluble in water but are soluble in nonpolar solvents. Solubility in both polar and nonpolar solvents is increased by the incorporation of unsaturated aliphatic or aromatic groups.

The most extensive uses of the quaternary ammonium compounds are based on their germicidal activity (129,138,146). As surgical germicides they are applied as hand and rubber-glove disinfectants, as sterilizers for surgical instruments, for wound irrigation, and as urinary antiseptics, as well as for special functions in obstetrics and gynecology, dermatology, ophthalmology, otology, and orology. Their utilization as general disinfectants is increasing in the sanitation of eating and drinking establishments, food-processing plants, and laundries. Quaternary ammonium compounds are employed to soften the "hand" of textiles, as flotation agents in froth flotation, as

mildew and mold inhibitors, and as surface-treating agents for plastics to inhibit the accumulation of static charges (129,130). The value of the quaternary ammonium compounds as corrosion inhibitors has been demonstrated recently in their application in secondary oil recovery, where they act, in addition, as bactericides (134).

#### MISCELLANEOUS DERIVATIVES

Numerous other nitrogen-containing fatty acid derivatives have been prepared and investigated. In general, these can be considered as derived from the amides or amines. At present, a number of such compounds are undergoing commercial development (stearanilide, polyoxyethylene amides, polyoxyethylene amines, and dodecylglycine). The oleic acid amide of *N*-methyltaurine,  $C_{17}H_{33}CON(CH_3)CH_2CH_2SO_3H$ , is used extensively as a surface-active agent in the textile field (136a).

#### Separation and Analysis

The methods for the separation, identification, and analysis of various fatty acids are still far from satisfactory. The analysis of mixed fatty acids is made difficult by the number of different acids present, their insolubility, and the fact that they are often closely situated members of homologous series. Various physical and chemical properties are determined in investigations of fatty acids and their mixtures. See also "Fractionation of fatty acids," p. 234.

The physical properties most commonly used for the purposes of identification and analysis of fatty acids and their esters are melting, freezing, transition, and boiling points, solubility, refractive index, density, x-ray diffraction spacing, spectral absorption (162), and optical rotation (see p. 181). The useful chemical properties include neutralization value, iodine, thiocyanogen, and hydrogen absorption, acetyl value, diene value, oxidation, and the ability to form various derivatives having additional characteristic properties. Some of the same tests are used for fatty acids and for fats and fatty oils (see p. 155).

No one of these methods should be relied upon solely for either identification of a fatty acid or its derivatives or the determination of their purity. They are particularly useful in the characterization and analysis of fatty acid mixtures and of highly purified fatty acids and their esters. The analysis is greatly simplified if the fatty acid mixtures obtained from fats and oils are fractionated by fractional distillation and crystallization and by chromatographic adsorption.

The **neutralization value** is defined as the number of milligrams of potassium hydroxide required to neutralize 1 gram of fatty acid and provides means of calculating mean molecular weight of mixtures.

The **iodine value** (I.V.) is the number of grams of iodine or equivalent halogen absorbed under standardized conditions by 100 grams of fat or fatty acid. It characterizes the true unsaturation of fatty acids only when the double bonds are nonconjugated, as halogen absorption is not quantitative in the case of conjugated fatty acids except when a suitable catalyst is present. For approximately complete saturation of the double bonds, the methods usually used are: the *Wijs method*, which depends upon the absorption of halogen by the fatty acid from an acetic acid solution of iodine monochloride; and the *Hanus method*, in which iodine monobromide is used in place of iodine monochloride. The Hanus test leads to results that are, in general, slightly higher than those of the Wijs method, especially in cases of high unsaturation. Many other iodine-value methods have been described in the technical literature, but for the

most part they find only limited application. The *Hübl method* and the *Rosenmund-Kühnemann method* are used extensively in Europe. The latter, when modified by adding mercuric acetate, gives quantitative results with eleostearic acid.

**Thiocyanogen Value.** Thiocyanogen,  $(\text{SCN})_2$ , adds directly to the double bonds of unsaturated fatty acids to form thiocyanogen derivatives, but to a different extent from the usual reagents for the determination of iodine. In general, the thiocyanogen radical, SCN, adds quantitatively to the single double bond of a monoethenoid acid, and almost quantitatively to one of the two double bonds of a nonconjugated diethenoid acid, and to two of the three double bonds of a nonconjugated triethenoid acid. The value is expressed in terms of the equivalent number of grams of iodine absorbed per 100 grams of sample. Since iodine adds quantitatively to all three types of acids named, the iodine and thiocyanogen values of a mixture of such acids are used in the calculation of the proportion of each acid present. Thus, from a knowledge of these two values, it is possible to calculate the percentages of oleic, linoleic, and saturated acids in the mixed fatty acids obtained from a natural oil or fat provided no other unsaturated acids are present. If the percentage of saturated acids and the iodine and thiocyanogen values are known, it is possible to calculate the percentages of oleic, linoleic, and linolenic acids present in the mixed fatty acids.

**Separation as Metallic Salts.** Many attempts have been made to develop quantitative methods of separating the individual fatty acids on the basis of the solubility of their metallic salts or soaps. The solubility of the salts, including those of the alkali metals (sodium, potassium, and lithium), the alkaline earth metals (calcium, magnesium, barium, and strontium), as well as the heavy metals (lead, zinc, iron, cobalt, nickel, mercury, gold, and silver), has been investigated in a variety of solvents, including methanol, ethyl alcohol, amyl alcohol, ethyl ether, acetone, benzene, toluene, and in mixtures of these and other solvents. However, no method has been developed that leads to effective quantitative separation of each component acid of mixtures such as are found in the ordinary fats and oils of commerce, but only to fractions that are more or less homogeneous with respect to certain types of acids.

The oldest and most widely used of the metallic-salt separation methods depends on the differential solubility in ethyl ether or ethyl alcohol of the specific lead soaps contained in a mixture of fatty acids. The method is employed primarily for the separation of saturated from unsaturated acids. The lead salt-ether method was first introduced in 1828 and has been adopted by the Association of Official Agricultural Chemists (153). Among the important modifications of this method is the one introduced by Twitchell and adopted by the American Oil Chemists' Society, which provides for the use of ethyl alcohol in place of ethyl ether (152). These so-called official methods are suitable for the quantitative separation of acids employing small samples (5-25 grams) of fats and oils.

The **acetyl value** and **hydroxyl value** are commonly determined in the examination of hydroxy acids and of fats and oils containing these acids. The acetyl value is defined as the number of milligrams of potassium hydroxide required for the neutralization of the acetic acid liberated on saponifying 1 gram of acylated sample. The hydroxyl value may be calculated from the same analytical data. It is the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 gram of sample. In addition to being present in natural hydroxy fatty acids, hydroxyl groups may be present as a result of oxidation or hydroxylation of the unsaturated bonds of a fatty acid.

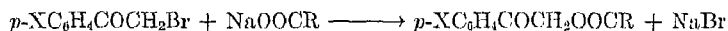
The **diene value** represents a special application of the Diels-Alder reaction for determining the number of conjugated double bonds in a fatty acid. It is based on the determination of the amount of maleic anhydride that reacts with a known weight of fatty acid or fat and is customarily expressed as the number of milliequivalents of iodine corresponding to the maleic anhydride that reacts with one gram of sample.

**Oxidation Methods.** Two quantitative methods of oxidation with aqueous potassium permanganate have been extensively applied in the analysis of fatty acids as well as of fats. The *Lapworth and Mottram method* is used for estimating oleic acid in crude oleic acid. The *Bertram method* is used for the determination of saturated fatty acids in the mixed fatty acids obtained from natural fats. Both of these methods, as more or less modified by later workers, are used widely in current investigations in many laboratories engaged in fat and oil research.

#### CHARACTERIZING DERIVATIVES

**Bromo Derivatives.** Most of the unsaturated fatty acids when treated in cold organic solvents, for example, chloroform or ethyl ether, add bromine at the double bonds to form bromo derivatives, which differ sufficiently in their solubility characteristics to permit separation of mixtures of the halogenated acids into individual components (158). For example, unsaturated fatty acids containing four or more double bonds form polybromides that are practically insoluble in almost all of the common organic solvents. Clupanodonic acid (containing five (or six) double bonds) forms a polybromide insoluble in nearly all organic solvents; arachidonic acid (containing four double bonds) forms an octabromide insoluble in cold ethyl ether and benzene. Linolenic acid forms a hexabromide that is insoluble in ethyl ether and many other solvents. Linoleic acid forms a tetrabromide that is soluble in ethyl ether but nearly insoluble in cold petroleum naphtha. Oleic, ricinoleic, erucic, and other monoethenoid acids form dibromides that are soluble in most of the common organic solvents.

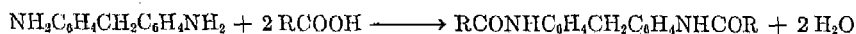
**Phenacyl Esters of Fatty Acids.** One of the earliest attempts to characterize the fatty acids systematically was by means of the phenacyl esters, including the *p*-bromo-, *p*-iodo-, and *p*-phenylphenacyl derivatives, formed as follows:



The *p*-bromo- and *p*-iodophenacyl esters of a number of saturated fatty acids, including both even- and odd-numbered members of the series, have been prepared. All of the acids from acetic to stearic give crystalline derivatives as indicated by the melting points (154). The melting points of the saturated acid derivatives increase with increase in the atomic weight of the halogen, but the melting points of individual members of the homologous series of acids were not sufficiently distinctive to permit their use as identifying criteria.

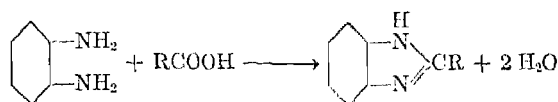
The *p*-phenylphenacyl esters of a series of octadecenoic acids were prepared with a view of obtaining derivatives that would be suitable for isolating and characterizing individual members of this series of acids. All of the derivatives possessed satisfactory melting points (155), but only the *p*-phenylphenacyl oleate and elaidate gave theoretical iodine values.

**Diamides of 4,4'-Liaminodiphenylmethane.** When fatty acids are heated with theoretical proportions of 4,4'-diaminodiphenylmethane (*p,p'*-methylenedianiline), diamides are formed, according to the following equation:



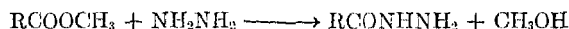
These amides have relatively high melting points and a sufficient temperature increment between adjacent members to render them valuable for purposes of characterizing fatty acids. All the saturated acids from acetic to stearic yield well-crystallized, relatively high-melting derivatives. The difference in melting points of the diamides of adjacent acids is relatively large for the lower members but becomes increasingly less as the series is ascended. Appreciable depression of the melting point occurs on addition of the diamide of the next higher homologous acid (160). The extent of the depression of the melting point also decreases as the series is ascended. Despite these limitations, the derivatives are especially useful for characterizing specific saturated acids.

**2-*n*-Alkylbenzimidazoles.** The 2-*n*-alkylbenzimidazoles of all the acids from formic to margaric have been prepared by reaction with *o*-phenylenediamine:



These derivatives are most useful for characterizing fatty acids, especially the lower members. They are readily prepared from small amounts of fatty acids and have comparatively high melting points. In the case of lower members, the melting-point interval between adjacent members is large and the depression in melting point resulting from the addition of the next higher homolog is considerable (159).

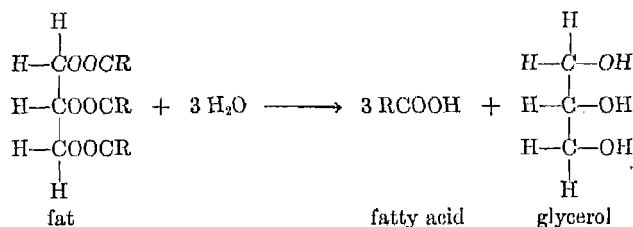
**Hydrazides.** Hydrazine,  $\text{NH}_2\text{NH}_2$ , reacts in a manner similar to ammonia with esters and acid chlorides to form hydrazides:



The hydrazides of the acids from formic to lauric have been prepared and characterized as well as those of myristic, palmitic, and stearic acids (156,161). The hydrazide of elaidic acid has also been prepared, but oleic acid under the same reaction conditions undergoes reduction and yields the hydrazide of stearic acid. The hydrazides are of value in identifying fatty acids, especially on the basis of their nitrogen contents, melting points, and mixed melting points.

### Manufacture from Fats

The manufacture of fatty acids from naturally occurring fat or oil is accomplished by one of several "splitting" or hydrolytic processes. Each of these processes brings about the primary hydrolysis reaction, which may be represented as follows:



In present-day manufacturing this reaction is carried out by either batch or continuous operation.

## BATCH PROCESS

*Caustic Splitting.* The earliest method for splitting fat was complete saponification using caustic, either sodium or potassium hydroxide (167). This process, one of the oldest chemical reactions known, is widely applied in soapmaking. Fat placed in a large steel kettle is blown with steam until the temperature reaches 80°C. Concentrated aqueous caustic is added gradually with continued addition of steam and with efficient agitation of the mass. Hydrolysis proceeds in stages, one fatty acid splitting off at a time until all three have been removed from the triglyceride molecule. The reaction is reversible and to prevent re-esterification the aqueous glycerol is periodically drawn off and replaced with fresh water and more caustic. The product, sodium or potassium soaps, must be acidified to free the fatty acid. This additional step and expense have relegated this method to only occasional use for the preparation of fatty acids. See also *Soap*.

*Twitchell Process.* The development by Twitchell in 1890 of a compound to catalyze the hydrolysis of fat led the way to the evolution of the method which is today the most popular of the fat-splitting processes (167). The Twitchell process involves first an acid wash with strong sulfuric acid to remove albuminous material and other impurities that are effective catalyst poisons. The fat is then mixed with 25–50% by weight of water and 0.75–1.25% of a Twitchell catalyst (originally “benzene-stearosulfonic acid,”  $C_6H_4(SO_3H)C_{18}H_{35}O_2$ , but most commonly a sulfonated petroleum product today). Sulfuric acid to the extent of about 0.5% based on the weight of fat is usually added with the Twitchell reagent. The mixture is boiled in an open tank with steam for 20–48 hours. The splitting is carried out, usually in covered tanks, in 2 to 4 stages, at the end of each of which the glycerol “sweet water” is withdrawn and replaced with fresh water or a less concentrated “sweet water” from a previous run. The effectiveness of the Twitchell reagent in bringing about the splitting is not entirely catalytic, but depends also on the emulsifying action of the substance. Its surface-active properties greatly increase the mutual solubility of the oil and water phases, and the establishment of an extensive oil–water interface accelerates the splitting reaction. Fatty acids produced by the Twitchell method are somewhat darker than those produced by continuous or batch high-pressure autoclave splitting.

*Autoclave Splitting.* Batch autoclave splitting either with or without catalyst is practiced to some degree, especially in Europe (167). It has certain advantages over the processes already described, primarily in the great reduction in the time required as well as the production of a lighter-colored fatty acid.

The reaction is accomplished in a copper or stainless-steel autoclave into which is charged the fat, 30–60% water, and, if catalytic, 1–2% of a catalyst, usually an oxide of calcium, magnesium, barium, or zinc. Steam is then admitted to achieve the desired pressure of 75–150 p.s.i. and a temperature of 300–350°F. when a catalyst is used. Hydrolysis is complete in 5–10 hours, after which the contents of the autoclave are blown into a separating tank where the glycerol is withdrawn from the fatty acid. An acid wash is essential to remove the catalyst, which is in combination with the fatty acid. Noncatalytic splitting requires a high-pressure autoclave, the temperature being increased to 450°F. and the pressure to 425–450 p.s.i. The reaction time is lowered considerably in this manner, requiring only 2–3 hours to effect 95–98% hydrolysis. This is possible because the reaction has a positive temperature coefficient and because the solubility of water in oil increases with temperature.

## CONTINUOUS PROCESSES

The process that seems destined to find the widest application for the production of fatty acids is continuous, countercurrent, high-temperature, high-pressure splitting (139,163,165,169,172,174,176). This method was developed during the 1940's by Colgate-Palmolive-Peet, Procter & Gamble, and Emery Industries and makes use of fatty-acid-resistant, high-pressure, stainless-steel alloys, which are now commercially available.

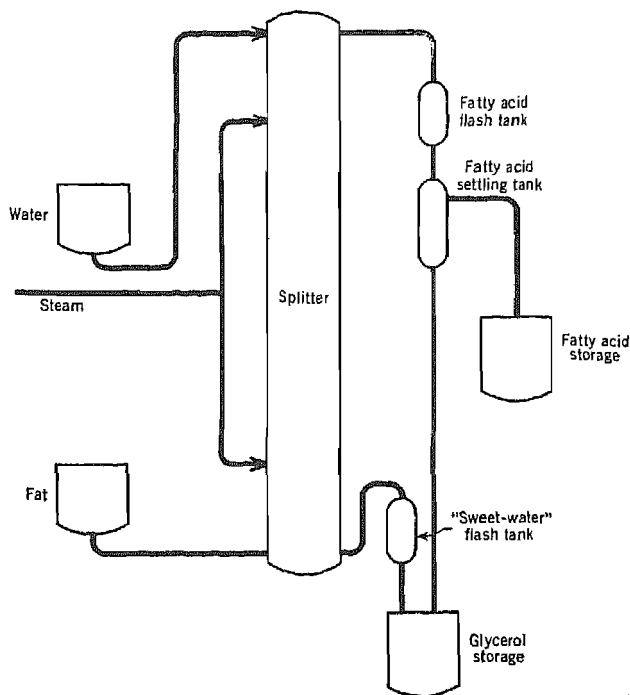


Fig. 23. Fat splitter.

A diagram of a typical continuous fat-hydrolysis plant is pictured in Figure 23. In the operation of such a unit, fat stock is pumped through a de-aerator to prevent darkening of the oil by oxidation during splitting. The feed stock is then pumped into the reaction chamber through a sparge ring, which breaks the fat into droplets. These droplets begin their rise through the aqueous glycerol in the "sweet-water"-accumulating section at the bottom of the column. As the oil rises it effectively sweeps entrained and dissolved fatty acid and oil from the countercurrent flow of "sweet water." Simultaneously, de-aerated water sparged into the top of the column is heated by contact with the fatty acids in the accumulator at the top of the column. As the droplets of water fall through the fatty acid layer, dissolved "sweet water" is swept out and carried downward. After the fat and water have left the contacting regions of the column, they are brought to hydrolysis temperature by the direct injection of steam at 240–250°C. and 650–700 p.s.i. Hydrolysis occurs in the emulsion or continuous-phase layer in the reaction zone of the column. The "sweet water" collected at the bottom is automatically discharged by an interface controller into a flash tank where a por-



tion of the water is removed. It is then piped to a settling tank and subsequently to a concentrator for processing to commercial glycerol. Discharge of the split acids from the top of the column is automatically controlled by a back-pressure valve, which also maintains proper operating pressure in the tower. The fatty acids pass into a flash tank where part of the entrained water is removed, and from there to a settling tank where further separation is effected.

The unit can be operated catalytically with an increase in capacity, using magnesium, zinc, or calcium oxide. In this case the product must be acid-washed to break down the soap.

Hydrolysis of fat by continuous methods is capable of producing a 97–99% split and a 10–25% “sweet water” at a rate of 3000–5000 lb. of fat per hour.

Continuous countercurrent splitting is not so satisfactory as batch processing for highly unsaturated fats such as fish oil, since a rather marked drop in iodine value occurs during hydrolysis.

Soapstocks, which result from the alkali refining of fats and oils, are also an important source for fatty acids. Upon acidulation the free acids are obtained and their separation into individual acids, when required, is effected in the same manner as the products of the processes just described.

#### FRACTIONATION OF FATTY ACIDS

The crude mixtures of fatty acids produced by any method are used as such for some purposes, but usually a separation of the mixture into the more useful component fatty acids is effected. The composition of the fatty acids obtained from the splitter is dependent on the fat or oil from which they were made and this composition dictates, to a large degree, the type of fractionation used. Fats and oils most commonly used for the production of fatty acids include coconut oil, palm oil, beef tallow, cottonseed oil, and soybean oil (see *Fats and fatty oils*).

The natural occurrence of a fat or fatty acid mixture whose composition is satisfactory for most uses is rare. Linseed, cottonseed, and soybean oils would possess more desirable drying qualities, for example, if the saturated content were reduced and the unsaturated content increased; and edible oils, such as lard and margarine, would have increased stability if the unsaturated acids were present in smaller amount (see also *Fats and fatty oils*).

In order to produce fatty acids containing specific chain lengths, a number of fractionation methods have been evolved.

*Crystallization.* One of the oldest processes, which is still widely practiced, is fractional crystallization of fatty acids, or “panning and pressing,” as it is known in the industry (166). This process is adaptable only to fatty acid mixtures such as tallow fatty acids, which solidify readily. The molten fatty acid mixture is run into flat pans and chilled to a specified temperature. The solid cakes are removed, wrapped in burlap bags, and pressed in a hydraulic press. This expression removes the liquid unsaturated acids, that is, the “red oil,” which constitutes the oleic acid of commerce (see p. 269). The residue from the pressing is single-pressed stearic acid. This residue can be re-formed into cakes and subjected to a hot pressing, with steam or hot-water heat, to produce double-pressed stearic acid. Cakes recast from this double-pressed acid when re-pressed at a still higher temperature yield triple-pressed stearic acid.

Fractional crystallization from solvents is a more recent method for the separa-

tion of fatty acids and is gaining widespread acceptance among fatty acid processors (139,166). Better separation is obtained and the process is well adapted to continuous operation. In practice, a solution of mixed fatty acids, usually in methanol or acetone, is passed through crystallizing tubes and then to continuous filters. From there the solid fraction is led into a stripping still to remove solvent and the filtrate into a second stripping still. The process is not adaptable to the effective separation from one another of the saturated fatty acids that do not vary greatly in chain length.

*Distillation.* The greatest technological advance in the fractionation of fatty acids has been made in the field of distillation (139,164,166,167,168,170,171,173,175). Overcoming the difficulties encountered in distilling a substance whose molecular weight averages about 200, whose boiling point at atmospheric pressure is well above its decomposition temperature, and whose character is acidic, has been an engineering triumph.

Batch-type stills were first applied to the separation of component fatty acids from mixtures, and are still in commercial use. The fatty acid mixture is charged into a direct-fired pot and subjected to superheated steam and a pressure of 150–200 mm. Hg. The low-boiling acids are flashed over and condensed and the high-boiling still bottoms are subsequently drawn off.

A refinement of this process currently employed for producing fatty acid blends introduces preheated (420°F.) fatty acid at the top of a vaporizing tower, whence it flows downward over trays countercurrent to superheated steam injected at the bottom of the tower. From the top of the tower fatty acid vapors pass to a condenser, which collects the acid but permits the accompanying steam to be removed by a multiple-stage high-vacuum unit. Unvaporized acids upon reaching the bottom of the tower are recirculated and nonvolatile pitch is discharged from the bottom of the tower. This material, called "fatty acid pitch" or "stearine pitch," containing polymers and decomposition products, has not found extensive application, but is used in certain types of paints and floor coverings.

A process for the continuous separation of fatty acid mixtures into component acids of 90% or better according to chain length is shown in Figure 24. Fatty acid feedstock enters the stripping tower after preheating in a heat exchanger. The acids flow downward over trays, encountering a rising column of vapors and steam, which serve to sweep air and moisture, as well as low-boiling fatty acids, from the descending stream. The ascending steam, air, and fatty acid vapors pass into a condenser where the acids are condensed and passed into the downtank, the steam and air being swept out through a catchall into a barometric condenser, which also maintains a pressure of about 50 mm. Hg in the stripping tower. From the downtank, a part of the fatty acid condensate is returned to the stripping tower as reflux, the balance being withdrawn as fraction 1.

The de-aerated and dried higher-boiling acids in tower 1 flow into the main fractionating section, tower 2, through a trap. Tower 2 is maintained at a pressure of 2 mm. Hg at the top and less than 32 mm. Hg near the bottom. The base of the tower is heated, usually with Dowtherm vapor, by a calandria-type heater. Vapors of lower-boiling fatty acids leave the top of the tower, are condensed, and a portion returned as reflux, the remainder being removed through a cooler as fraction 2. Bottoms from this tower, consisting of high-boiling acids, flow into the flash drum, where upon further heating they are vaporized and flow out the top of the tower. These vapors when condensed and cooled are removed as fraction 3. Bottoms from the flash

drum are returned to the stripping tower where they are reworked. The bottoms from this tower are removed as pitch.

Operating conditions for the system are dependent upon the composition of the fatty acid feedstock. The design of the main fractionating tower can be varied to

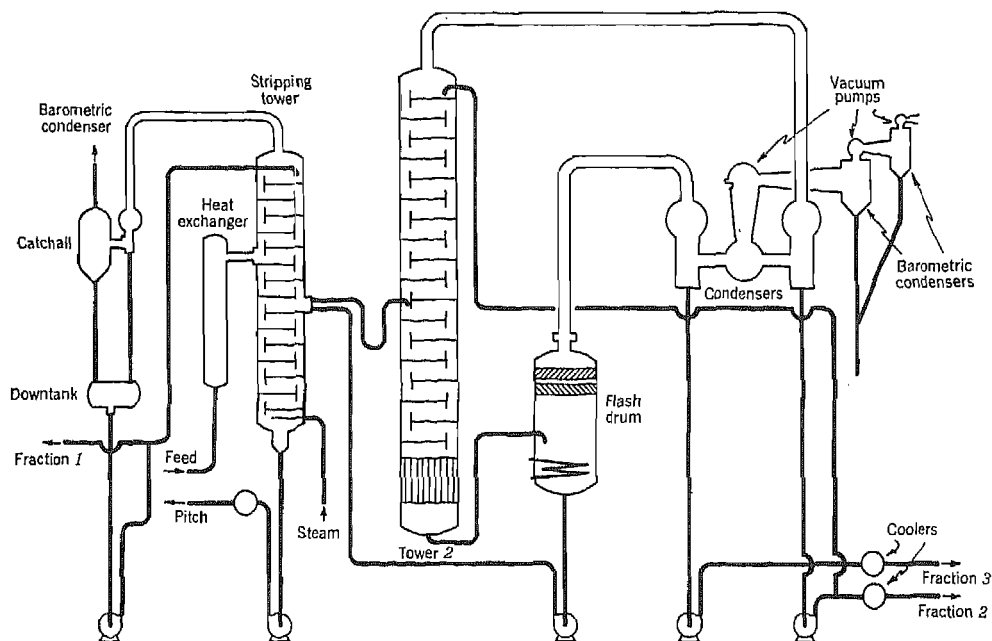


Fig. 24. Fatty acid fractionating still.

produce fractions of various compositions, but general practice has been to design for a purity of 85-90% in each fraction.

#### ECONOMIC ASPECTS

In addition to the products sold under the names of individual acids (as lauric, palmitic, stearic, oleic, oleic-linoleic, and ricinoleic acids), mixtures of fatty acids from various sources are on the market. Among these mixed acids, usually single- or double-distilled, are coconut, palm, cottonseed, corn, soybean, linseed, tung, castor, and tallow and animal fatty acids.

The solid products are supplied in powder, flake, or slab form; the containers are bags, drums, or tank cars.

Although no figures are available on the present total production of fatty acids, some 500,000,000 lb. a year are said to have been used by the U.S. industry during World War II, with production increasing steadily since then.

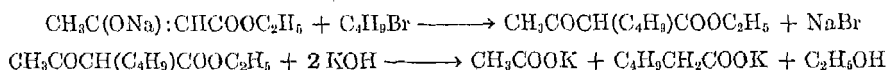
The following figures from the U.S. Department of Commerce (*Bureau of Census Report*, MC28G) indicate the recent growth of the U.S. fatty acid industry:

	1939	1947
Number of producers.....	9	16
Number of employees (average).....	—	1,335
Cost of materials, fuel, electricity, etc.....	\$6,650,000	\$50,943,000
Value of products shipped.....	\$9,463,000	\$68,094,000

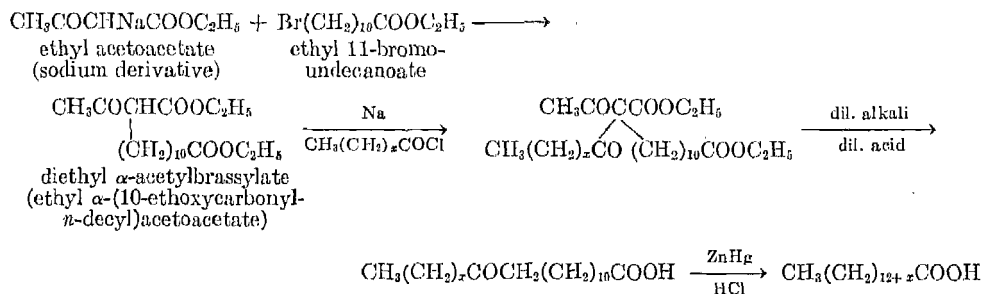
## SATURATED ACIDS

*Acetoacetic Ester Synthesis.* This method is especially useful in the synthesis of the intermediate and higher aliphatic acids. Thus, the sodium derivative of acetoacetic ester on treatment with absolute alcohol and *n*-butyl bromide forms ethyl *n*-

butyl acetoacetate, which on heating with alcoholic potassium hydroxide yields the potassium salts of acetic acid and *n*-butylacetic or caproic acid:



*Robinson-Robinson Synthesis.* Developed originally for the preparation of the higher aliphatic keto acids, this method in the course of its various modifications has become of first importance as a means of obtaining many of the long-chain aliphatic acids (181). It represented originally a modification of the malonic ester synthesis and later of the acetoacetic ester synthesis. Thus, the sodium derivative of an  $\alpha$ -substituted acetoacetate (obtained from ethyl acetoacetate and an  $\omega$ -bromo acid ester,  $\text{Br}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$  (180)) reacts with a fatty acid chloride to give a long-chain  $\alpha$ -acylacetoacetate containing a second ester group. This reaction product can undergo stepwise hydrolysis in such a way as to remove the acyl group corresponding to the stronger acid; the remaining keto acid can be reduced to the desired saturated acid by the Clemmensen method:



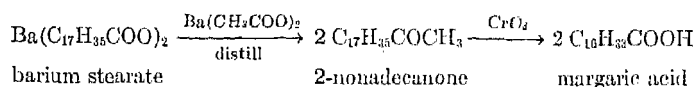
Diethyl  $\alpha$ -acetylbrassylate is obtained in good yield from the readily available 11-bromoundecanoic ester. The complex resulting from the condensation of the sodium derivative of diethyl  $\alpha$ -acetylbrassylate with an acid chloride, when submitted to a stepwise hydrolysis, yields the desired long-chain keto acid accompanied by varying amounts of 13-ketotetradecanoic acid. These higher keto acids are readily reduced by the Clemmensen method, and thereby twelve carbon atoms are added at a time to the original acid. By this method, stearic acid through its acid chloride yields triacontanoic acid, and undecanoic and lauric acids yield tricosanoic and tetracosanoic acids, respectively. Similarly, by starting with behenoyl chloride, tetratriacontanoic acid and then hexatetracontanoic acid have been synthesized.

*Grignard Reaction.* Although the addition of a carbon atom by the reaction of a Grignard reagent with carbon dioxide in acid solution is more useful for the preparation of lower fatty acids than higher (because of the greater ease of preparation of the Grignard reagents), several higher acids have been prepared by this method.  $\gamma$ -Keto acids can be obtained by treating a Grignard reagent with *N*-methylsuccinimide,  $\text{OC}(\text{CH}_2)_2\text{CONCH}_3$ , and hydrolyzing the resulting 1-methyl-5-alkyl-2(5*H*)-pyrrolone.

Reduction of the keto acids gives the parent acids, which contain four carbon atoms more than the Grignard reagent; the acids from caproic to capric have been prepared in this way (179).

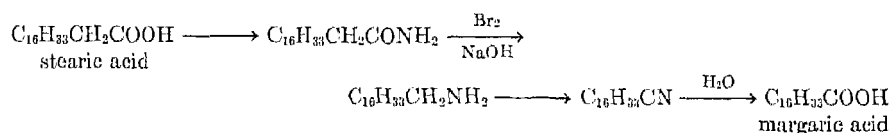
*Pyrolysis of Barium Salts.* One of the oldest methods of producing fatty acids of shorter chain length than the original acid involves the pyrolysis of the barium salts of

the higher acids in the presence of barium acetate to an alkyl methyl ketone, which on oxidation yields the next lower homologous acid:



Margaric acid by the same reaction yields palmitic acid. However, the yields from this method are comparatively poor.

*Hofmann Rearrangement of Amides.* The rearrangement of an amide to an amine (with the loss of carbon dioxide) by treatment with excess bromine and alkali is followed by oxidation of the amine by the bromine present to the corresponding nitrile, which can be hydrolyzed to the acid. For example:



Although the yields of amines above  $\text{C}_6$  are poor, stearic acid has been converted by this method to margaric acid and the latter to palmitic acid, and so on to pelargonic acid.

*Degradation of  $\alpha$ -Hydroxy or  $\alpha$ -Halo Acids.* Heating or distilling an  $\alpha$ -hydroxy acid or its lactide forms the next lower unsubstituted aldehyde, which can then be oxidized to the acid. The same products can be obtained by direct oxidation of  $\alpha$ -hydroxy acids by potassium permanganate in acetone solution. Thus, margaric acid has been prepared from stearic acid by both of these methods.

$\alpha$ -Chloro or  $\alpha$ -bromo acids on fusion with alkali yield the next lower unsubstituted acids; 2 chloroundecanoic acid, for example, gives decanoic acid.

*Oxidation of Alcohols or Aldehydes.* When the alcohol or aldehyde is available, the corresponding fatty acid may be obtained by simple oxidation. Some higher unsaturated aldehydes can be prepared by condensation of crotonaldehyde,  $\text{CH}_3\text{CH}:\text{CHCHO}$ , in the presence of piperidine acetate: octatrienal,  $\text{CH}_3(\text{CH}:\text{CH})_3\text{CHO}$ ; dodecapentaenal,  $\text{CH}_3(\text{CH}:\text{CH})_5\text{CHO}$ ; and hexadecaheptaenal,  $\text{CH}_3(\text{CH}:\text{CH})_7\text{CHO}$ . The aldehydes can be reduced to saturated alcohols, which can be oxidized to acids. Dodecapentaenal forms lauraldehyde and then lauric acid. On the other hand, the malonic acid condensation product of dodecapentaenal gives tetradecaheptaenoic acid,  $\text{CH}_3(\text{CH}:\text{CH})_6\text{COOH}$ , which can be reduced to myristic acid. Hexadecaheptaenal similarly can yield cetyl alcohol and then palmitic acid, and the malonic acid condensation product of hexadecaheptaenal can be hydrogenated and distilled to produce stearic acid.

**Synthesis of Fatty Acids from Hydrocarbons.** Large-scale production of fatty acids by air oxidation of paraffins was developed in Germany during World War II (182,183), whereas in the U.S. this process has been directed to the production of a mixture of acids, alcohols, ketones, etc.

Oxidation of paraffins by air in the presence of permanganate catalysts was operated on a large scale in Germany throughout the war, although there is some doubt that the claimed productions of 60,000 tons of fatty acids in 1940 and 100,000 tons in 1944 were actually achieved. The four plants, located at Magdeburg, Witten/Ruhr, Heydebreck, and Ludwigshafen-Oppau in Germany, probably had a combined maxi-

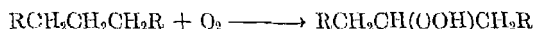
num capacity of approximately 100,000 tons of fatty acids of various types and qualities.

A method (called the "oxo process") was also developed in Germany for producing fatty alcohols and acids by the catalytic reaction of monoolefins with water gas under pressure; in the U.S. this process is being applied to the synthesis of aldehydes and a few higher alcohols. Commercial production of fatty acids from olefins was not achieved in Germany by the time hostilities ceased, although a plant with an estimated capacity of 10,000 tons annually of synthetic alcohols was erected and would have been in operation in a short time. See *Oxo and oxyl processes*.

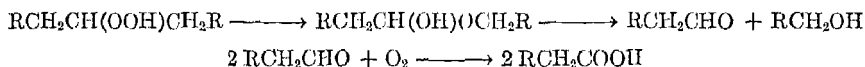
*Synthesis from Paraffins.* Experimental production of synthetic fatty acids by oxidation of paraffin hydrocarbons began about 1936 and reached full commercial production in 1939.

Any saturated paraffin fraction of the appropriate molecular weight can be used in the air-oxidation process. These paraffin or Gatsch fractions having a mean molecular weight of 280-290 may be obtained by hydrogenation (*q.v.*) of coal or by the Fischer-Tropsch synthesis (see *Fuels, synthetic liquid*). Generally, only the fatty acids derived from oxidation of the Fischer-Tropsch Gatsch fraction (so-called Fischer Gatsch) have been used for the production of edible fats, but consumption has not exceeded 5% of the production of fatty acids from this source. The remainder has been used primarily in the manufacture of soaps. For soapmaking purposes, the most desirable fraction contains hydrocarbons varying from  $C_{18}H_{38}$  to  $C_{28}H_{58}$  with an average molecular weight of 284.

The actual oxidation step is relatively simple and consists essentially of bringing paraffins into contact with air in the presence of a suitable catalyst, generally potassium permanganate or a manganese soap such as manganese stearate. Although the exact mechanism by which oxidation occurs is unknown, it is believed that oxygen adds at various positions along the carbon chain to form hydroperoxides:



These hydroperoxides, being unstable, are converted successively to alcohols, aldehydes, and fatty acids, presumably as follows:



Apparently, other reactions also occur and the final reaction product consists of a complex mixture of unreacted paraffins, aldehydes, alcohols, ketones, fatty acids, hydroxy acids, esters, and other products. By separating and recycling the unreacted paraffins, about 80% of the original paraffin is ultimately recovered as fatty acids. The composition of the recovered fatty acids apparently varies considerably with the conditions of oxidation and subsequent fractionation. On a commercial scale, four major fractions are generally produced, which are claimed to be essentially as follows:  $C_4$  to  $C_{10}$ , 12%;  $C_8$  to  $C_{20}$ , 65%;  $C_{20}$  to  $C_{28}$ , 14%; residue,  $C_{28}$  and above, 9%.

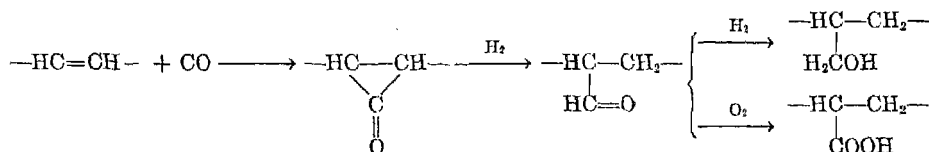
In actual practice, the hot raw material (Fischer Gatsch fraction, b.p. 320-450°C.) is first centrifuged to remove any foreign solids, after which it is charged into the oxidation towers. These are cylindrical vessels of 10-12 tons in capacity, made of aluminum, 1.8-2.3 meters in diameter, and 10 meters high. The converter contains a mushroom-shaped false bottom perforated with about 1000 holes,  $\frac{1}{16}$  in. in diameter. The bottom of the converter contains an aluminum heating coil and, about midway to the top, a cooling coil of the same material. The top of the converter is connected by means of a large vapor duct to a surface and then to a barometric condenser.

The catalyst, generally a 0.2% solution of potassium permanganate in water, is prepared in 500-gal. tanks equipped with stirrers. In one variation of the oxidation process, the paraffins may first be activated by mixing them with powdered potassium permanganate and heating to 150°C. for 10 minutes. Where this step is omitted, the potassium permanganate solution is charged to the converter containing the paraffin and the mixture is heated to 110°C. to drive off the moisture. Air is then blown through the charge at the rate of about 50 cu.m. per hour per ton of charge. Since the reaction is exothermic, liberating approximately 500 cal./kg. paraffin, the charge must be cooled in order to maintain the preferred temperature of approximately 105°C. The aeration is continued for 20 hours, when the reaction product will contain 33-35% of free fatty acids. By recycling the unreacted paraffin, the final overall yield of fatty acids is about 80%.

The oxidate is washed with hot water to remove the water-soluble acids and catalyst, after which the residue is saponified at a temperature of 100°C., using direct steam. After standing about 10 hours, the product separates into two layers consisting of about  $\frac{2}{3}$  soap and emulsified unsaponifiable materials and  $\frac{1}{3}$  unreacted paraffins. The latter are recycled to the converter. The other fraction is pumped continuously through an autoclave heated under pressure to 180°C. to break the emulsion, and then to continuous separators. About  $\frac{1}{4}$  of the separated product at this stage is unreacted paraffin, which is also returned to the converter.

The remaining oxidate is further freed of unsaponifiable matter by flash distillation. This is accomplished by heating the mixture under pressure to 320–380°C. in a gas-fired pipe still, adding steam and flashing into a baffled dephlegmating chamber at atmospheric pressure. The paraffin vapors pass to a condenser and are recycled to the converter. The soaps settle to the bottom of the chamber and are removed by means of a screw conveyor to solution tanks where they are dissolved in water and then acidulated.

**Synthesis from Olefins.** The oxo process for the production of fatty alcohols and acids from olefins was operated in Germany on a pilot-plant scale (3 tons per day) for several years. The necessary olefins may be produced either by cracking heavier paraffin fractions derived from the normal Fischer-Tropsch synthesis or by operating the Fischer-Tropsch process so as to produce a high ratio of olefins to paraffins. Regardless of the source of the olefins, the subsequent steps in the synthesis are the same. The olefins are further treated with water gas in the presence of the Fischer-Tropsch catalyst (90% cobalt, 7% thorium, and 3% magnesia, deposited as carbonates on kieselguhr), which results in the introduction of carbon monoxide at the double bonds to form unstable cyclic ketones. The ketones are subsequently reduced by the hydrogen to the corresponding aldehydes, which may then be further reduced in the presence of Raney nickel to the corresponding alcohols or oxidized in the presence of sodium carbonate to acids. The reactions may be represented as follows:



Only primary alcohols are formed on reduction of the cyclic ketone, but since the double bond in the original olefin may be located anywhere along the hydrocarbon chain, the final hydrogenation product will consist of a mixture of normal and iso alcohols.

The  $\text{C}_{11}$  to  $\text{C}_{17}$  fractions of olefins derived either from cracked paraffins or by direct synthesis from water gas are introduced into vertical converters consisting of cylinders 400 mm. in diameter and 12 meters high. For purposes of heating and especially cooling the charge, since the reaction is highly exothermic, each converter is provided with a bundle of 30 tubes, 30 mm. inner diameter and 38 mm. outer diameter, which extend  $\frac{3}{4}$  of the distance from the bottom of the chamber. Each converter is also provided with a reflux condenser to return any hydrocarbon or aldehyde that may be carried out by the gas.

A suspension of catalyst and liquid olefins, or of catalyst and Diesel oil if the reaction is to be carried out with gaseous olefins, is made by agitation in a mixing vessel and then pumped to a high-pressure measuring tank from which it is charged to the converter to a depth of about  $\frac{3}{4}$  of its height or 720–840 liters, approximately 500–600 kg. of product.

Water gas, freed of impurities and especially of organic and inorganic sulfur to which the catalyst is extremely sensitive, is compressed to 200–300 atm. in a four-stage system of compressors, and is then reduced to 150 atm. and introduced into the bottom of the converter containing the reacting mass preheated to 150°C. The water gas is supplied for 20–30 minutes and the temperature maintained at 150–180°C. The relative amounts of aldehydes and ketones formed are primarily a function of the temperature of operation. The higher temperature, although favoring aldehyde production, also favors subsequent polymerization and so reduces the final yield of aldehydes. For example, with ethylene, temperatures as low as 85°C. can be used and under optimum conditions the reaction product is composed of 70% of propionaldehyde and 30% of diethyl ketone by weight.

The water gas, which originally has a composition of 13% carbon dioxide and inerts, 38–39% carbon monoxide, and 48–49% hydrogen, is recycled through the converter after addition of fresh gas, usually in the ratio of 200 cu.m./hour of exhaust gas and 40–50 cu.m./hour of fresh gas. The final



residual gas is exhausted and burned when the concentration of inert gases reaches approximately 30% and carbon monoxide and hydrogen, 15–20% and 40–50%, respectively. The catalyst may be re-used 50 to 100 times, depending on the type of olefins with which it is employed.

Since it is not possible to separate the various aldehydes and unreacted olefins by distillation because of the tendency for aldehydes to undergo polymerization, the catalyst is removed and the reaction product is hydrogenated in the presence of Raney nickel to convert the aldehydes to alcohols and the residual olefins to paraffins. The product from the second stage of the reaction is then fractionally distilled to separate the alcohols and paraffin hydrocarbons. The higher alcohols are subsequently sulfonated for the production of various detergent products and the paraffins are either used as such or returned to the Fischer-Tropsch plant.

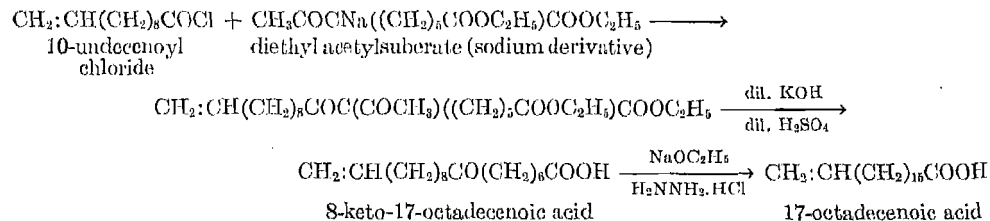
### UNSATURATED ACIDS

No general methods are available for the synthesis of unsaturated acids that are applicable for preparing an extensive homologous series of these compounds. Dehydrobromination of monobromo acids or dehydration of monohydroxy acids, except  $\alpha$ - and  $\omega$ -substituted acids, generally leads to mixtures of at least two positional isomers; consequently, even specific short-chain unsaturated acids are prepared by methods of limited applicability. With increasing chain length, synthesis of specific monounsaturated acids becomes increasingly difficult and the synthesis of polyunsaturated acids even more so.

Many of the described syntheses are either partial syntheses or lead to a mixture of *cis* and *trans* isomers. 10-Ketostearic acid, for example, can be obtained by the Robinson-Robinson synthesis (181), and can in turn be converted into oleic and elaidic acids through 10-hydroxystearic and 10-iodostearic acids (p. 555 of ref. 6).

A mixture of oleic (35%) and elaidic (65%) acids was also obtained by malonic ester synthesis from 1-iodo-7-hexadecene,  $\text{I}(\text{CH}_2)_6\text{CH}:\text{CH}(\text{CH}_2)_7\text{CH}_3$ , in *n*-butyl alcohol, and 5-undecenoic, 6-dodecenoic, and palmitoleic acids were similarly prepared (178).

Two positional isomers of ordinary oleic acid, namely, 16- and 17-octadecenoic acids, were prepared by synthesizing the unsaturated keto acids by means of the acetoacetic ester method and reducing them by the Wolff-Kishner method. 10-Undecenoic acid was converted to 10-undecenoyl chloride and condensed with the sodium derivative of diethyl acetylsuberate; the condensation product was hydrolyzed by the Robinson-Robinson stepwise procedure to give 8-keto-17-octadecenoic acid, which was reduced to 17-octadecenoic acid, m.p. 55.0–55.5°C.:



Synthesis of 16-octadecenoic acid, m.p. 62.8–63.5°C., was accomplished in the same manner using 9-undecenoyl chloride instead of 10-undecenoyl chloride (106).

Ethenoid acids can also be obtained by hydrogenation of acids containing additional double bonds or of acids containing triple bonds. In selective hydrogenation of polyethenoid acids, migration of double bonds may take place, and furthermore a very large proportion of the double bonds are converted from the *cis* to the *trans* configuration. Acetylenic acids have been reduced in various ways. Thus, 11-octa-

decynoic acid (formed by the reaction of 1-chloro-10-heptadecyne with excess sodium cyanide in 75% alcohol and hydrolysis of the nitrile with sodium hydroxide) was reduced with Raney nickel under a pressure of 50 p.s.i. until the theoretical amount of hydrogen was absorbed. The resulting 11-octadecenoic acid was the cis isomer and was converted to the trans (vaccenic acid) by heating with powdered selenium for 7 minutes at 180–200°C. (177). Acetylenic acids can also be converted to ethylenic acids by reaction with hydriodic acid and reduction of the product with zinc in acetic acid solution. Mild reduction of behenic acid,  $\text{CH}_3(\text{CH}_2)_7\text{C}\equiv\text{C}(\text{CH}_2)_{11}\text{COOH}$ , produces erucic acid (cis), while more vigorous treatment gives brassidic acid (trans).

The general processes by which isomeric unsaturated acids may be produced include: (1) hydrogenation of more highly unsaturated acids; (2) isomerization, as by action of heat and isomerization catalysts; (3) dehalogenation or dehydrohalogenation of saturated halo acids; and (4) dehydration of hydroxy acids (as ricinoleic acid with the formation of a second double bond to give linoleic isomers), by the action of heat and dehydration catalysts. For example, 2-octadecenoic acid has been prepared from 2-bromostearic acid (formed by bromination of stearic acid) by treatment with alcoholic potassium hydroxide. 3-Octadecenoic acid can be prepared from the 2-isomer by treatment with hydriodic acid and heating with alcoholic potassium hydroxide, and the 4-isomer similarly from the 3-, and so on.

The most generally used method for preparing acetylenic acids is the removal of hydrogen halide from dibromides or diiodides of ethylenic acids (dibromo saturated acids), usually with alcoholic potassium hydroxide. Stearolic acid (9-octadecynoic acid) results in this way from oleic or elaidic dibromide (9,10-dibromostearic acid), and behenic acid from erucic or brassidic dibromide. Several isomers of the naturally occurring 6-octadecynoic acid (tariric acid) have been prepared by adding hydriodic acid and treating the dihydriodide with alcoholic potassium hydroxide; this results in a displacement of the triple bond in one direction or the other, and by repeating the operation with the new isomer, a series of octadecynoic acids can be prepared. Chain lengths can be increased by nitrile formation (p. 237) and (for the preparation of 2-acetylenic acids) by reaction of a substituted acetylide,  $\text{RC}\equiv\text{CNa}$ , with carbon dioxide in the presence of anhydrous ether.

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K. S. MARKLEY  
 R. T. O'CONNOR (Spectral Properties)  
 M. E. JEFFERSON (Crystal Properties)  
 H. J. HARWOOD AND E. F. BINKERD (Nitrogen Derivatives;  
 Manufacture from Fats)  
 T. H. HOPPER (Separation and Analysis)

### STRAIGHT-CHAIN SATURATED ACIDS

For the lower saturated fatty acids, see *Acetic acid*; *Butyric acid*; *Formic acid*; *Propionic acid*.

#### Valeric Acid, $C_5H_{10}O_2$ .

Valeric acid (*n*-valeric acid) is a colorless liquid with a putrid odor; its solubility in water is 3.7 grams/100 grams at 16°C. It has been reported to occur in the oils of valerian root, pineapple (3), and *Artemisia verlotorum* (2). However, these reports are questionable and require further verification in view of the fact that two of the three isomeric branched-chain acids have also been reported to occur naturally and it is difficult to separate and identify the individual acids or their esters. See " $\alpha$ -Methylbutyric acid," "Isovaleric acid," "Pivalic acid." *n*-Valeric acid has been found in pyroligneous acid, in petroleum distillates, and in raw cracked gasoline. Valeric acid is obtained with other fatty acids from the oxidation of stearic acid and of castor oil. It is also formed during the fermentation of calcium lactate and of cellulosic and hemi-cellulosic materials or their hydrolyzates (7), and by the bacterial oxidation of cyclohexane (4). A kaoliang fusel oil is reported to contain 53% of valeric acid. This acid is the main constituent of the excretions of *Ascaris lumbricoides* (6).

Methods of preparing valeric acid by the action of carbon dioxide and water on olefins, by reaction of formic acid with butene, and by the electrolytic oxidation of 1-pentanol have been patented. It can be obtained also by the oxidation of high-molecular synthetic paraffins (1).

Valeric acid is used as an intermediate. Its  $\alpha$ -hydroxy derivative is an effective aerial disinfectant (5).

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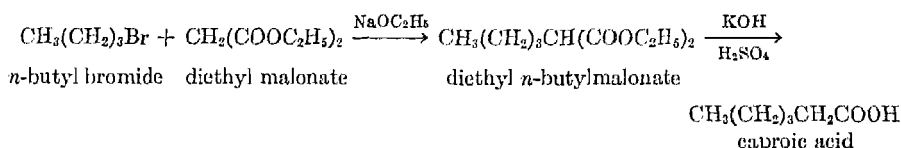
MABEL D. REINER

**Caproic Acid,  $C_6H_{12}O_2$ .**

Caproic acid is a colorless liquid with an odor characteristic of goats, from which it gets its name. Caproic acid is only slightly soluble in water (see p. 186).

Caproic acid occurs naturally in small amounts as the glyceride in goat's milk, coconut oil, various palm oils, and other oils. It was first isolated by Chevreul in 1816 from butterfat. One of the causes of rancidity in edible fats, such as butter, is the oxidation of caproic acid by microorganisms to form methyl *n*-propyl ketone, which has a pungent, unpleasant odor.

Caproic acid is made commercially by the oxidation of *n*-hexyl alcohol and by the hydrolysis of capronitrile (pentyl cyanide, obtained from 1-pentanol). Caproic acid can also be made by the malonic ester synthesis starting with *n*-butyl bromide (1):



Similarly, the acetoacetic ester synthesis starting with *n*-butyl bromide yields caproic acid. It can also be produced by the oxidation of 2-octanol (capryl alcohol) obtained from castor oil (2).

Caproic acid is particularly suitable for the introduction of the *n*-hexyl group into pharmaceuticals and related products. For example, it esterifies with phenols to form caproates, which can rearrange to form hexylphenols. On reaction with resorcinol in the presence of a condensing agent such as zinc chloride, caproic acid yields an intermediate ketone that can be reduced to hexylresorcinol, which has marked germicidal properties and a phenol coefficient over 50. The ethyl, amyl, and allyl esters of caproic acid are used as synthetic flavors. A lithium salt has been suggested as a thickener for mineral or vegetable lubricating oils (3).

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J. A. FIELD

**Enanthic Acid,  $C_7H_{14}O_2$ .**

Although enanthic acid (enanthylic acid) has been reported in floral waxes and in the oil of the violet leaf and of calamus, it is not definitely known to be present in naturally occurring oils, fats, and waxes. Enanthic acid has been identified in rancid oils, in the pyrolytic products of shark oils, in a petroleum distillate (10), and in appreciable amounts in various fusel oils. It is an oily liquid with a rancid odor.

The most satisfactory methods for the preparation of enanthic acid are the oxidation of heptanal with: (1) pure oxygen in the presence of a catalyst (94.5% yield) (8); (2) sulfuric acid in the presence of aluminum heptoxide,  $Al(OC_7H_{15})_3$  (94.3% of 99.7% purity) (2); and (3) potassium permanganate in acid solution (76-78% yield of 95-97% purity) (7). It is also formed during the cracking of cottonseed oil and from the oxidation of 7-pentadecene (9) and of high-molecular synthetic paraffins (1).



Enanthic acid has growth-inhibiting properties against microorganisms (3,4,6) and fungistatic activity (5). It is used as an intermediate in organic syntheses.

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MAUEL D. REINER

### Caprylic Acid, $C_8H_{16}O_2$ .

Caprylic acid is found widely distributed in both animal and vegetable oils and fats, invariably as a minor component, rarely comprising more than 10% of the fatty acid content. Coconut and similar oils and milk fats are the chief sources of caprylic acid, but it is present also in lesser amounts in rarer oils such as grapefruit-seed oil, oil of sweet oranges, grape-seed oil, and others. Caprylic acid is a colorless liquid with a persistent rancid odor.

Caprylic acid has not achieved the commercial importance of longer-chained acids, and is marketed primarily as a chemical intermediate. It is commercially available as a fractionally distilled product of 90% purity. The price of caprylic acid varied between 30 and 50¢/lb. over the ten-year period 1939-49. See also "Manufacture from fats," p. 231.

H. J. HARWOOD AND E. F. BINKERD

### Pelargonic Acid, $C_9H_{18}O_2$ .

Pelargonic acid has been found in minute amounts in the fat of human hair (1). This is the first definite report that a straight-chain, odd-numbered-carbon fatty acid was obtained from a natural source (1). Its presence in the oils of rue, lavender, and of *Pelargonium roseum* and in Japan wax had been reported, but it was probably formed during the oxidative cleavage of the unsaturated acids in these oils. It has been found in a petroleum distillate, in rancid fats, and in fusel oil from beets, potatoes, and cane molasses. Pelargonic acid is an oily liquid with a heavy rancid odor.

Pelargonic acid is prepared by oxidizing oleic acid (4) and sulfated oleic acid or sulfated methyl oleate (2). It is also formed by the oxidation of undecane with nitrogen dioxide.

Pelargonic acid is claimed to be an insect repellent (3). The product of its reac-

tion with zein is suitable for curing and molding (5). Esters of pelargonic acid with some alcohols give compounds having various industrial uses.

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MABEL D. REINER

### Capric Acid, $C_{10}H_{20}O_2$ .

Capric acid is found as a minor component in the same fats and oils that are the sources of caprylic acid, primarily coconut oil and milk fats. Unlike caprylic acid, capric acid does comprise a major component of certain oils, elm-seed oil containing 50% and California-bay-tree-seed oil, 37%. However, capric acid is usually produced commercially from coconut oil. Capric acid is a low-melting solid with a somewhat rancid odor.

Capric acid is marketed chiefly as an intermediate for chemical syntheses. It is available as a fractionally distilled product of 90% purity. The price of capric acid varied between 30 and 50¢/lb. over the ten-year period 1939-49. See also "Manufacture from fats," p. 231.

H. J. HARWOOD AND E. F. BINKERD

### Undecylic Acid, $C_{11}H_{22}O_2$ .

*n*-Undecylic acid is said to be present in small percentages in oil of iris. It is a crystalline solid with a rather pleasant odor, which distinguishes it from the lower saturated acids. The acid is commercially available as a product of the catalytic hydrogenation of 10-undecylenic acid. On a laboratory scale, undecylic acid may be synthesized from commercially available *n*-decyl alcohol by conversion to the bromide or iodide, and then to undecanenitrile, which is hydrolyzed to undecylic acid. It was originally described by Krafft, who reduced 10-undecylenic acid with red phosphorus and hydrogen iodide. Other methods of preparation include fusion of 2-bromolauric acid with potassium hydroxide (1) and oxidation of methyl *n*-undecyl ketone. It is one of the oxidation products of paraffin.

Undecylic acid is a powerful bactericide. Undissociated molecules of the acid have a remarkable sterilizing action against putrefactive bacteria (2).

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M. G. GERGEL AND MAX REVELISE

**Lauric Acid,  $C_{12}H_{24}O_2$ .**

Lauric acid is the lowest saturated fatty acid found abundantly in nature. It is a major constituent of palm-kernel oils. Coconut oil, the principal commercial source, contains approximately 50% lauric acid. It is also found in the seed fats of plants of the laurel family and in milk fat. Lauric acid is a crystalline solid with a faint fatty odor.

Lauric acid is usually utilized as the mixture of acids obtained from coconut oil, or as the "topped" mixture from which the caproic, caprylic, and capric acids have been removed by distillation. It is also commercially available as a fractionally distilled product of 90% purity. The price of lauric acid fluctuates with the price of coconut oil, fractionated lauric acid varying between 25 and 45¢/lb. in the ten years from 1939 to 1949. The price quoted in June 1950 for the commercially pure acid was 32¢/lb. for carload lots. See also "Manufacture from fats," p. 231.

Metallic salts of lauric acid are perhaps the most useful of its derivatives (see *Driers and metallic soaps*). Nonmetallic soaps, particularly ethanolamine types, are extensively employed as detergents and emulsifiers. Esters of lauric acid (see *Esters, organic*) find application as plasticizers, as emulsifying agents, and in protective coatings. Lauroyl chloride, prepared by the chlorination of lauric acid with phosphorus trichloride, thionyl chloride, or phosgene, is used as an intermediate in the preparation of esters and amides. Lauryl alcohol (see Vol. 1, p. 319), prepared by the reduction of lauric acid or one of its esters, after sulfation forms the active ingredient of certain popular detergents.

Nitrogen derivatives of lauric acid, lauramide and laurionitrile, are substances of increasing importance (see p. 221). *n*-Dodecylamine, prepared by the reduction of laurionitrile, is utilized in the production of highly germicidal quaternary ammonium salts (see *Quaternary ammonium compounds*) and other surface-active materials (*q.v.*). Many of the properties of the long alkyl chains reach a peak at twelve carbon atoms. For this reason, lauric acid derivatives are of particular value in many fields. The extent of their use is limited only by their availability.

H. J. HARWOOD AND E. F. BINKERD

**Tridecanoic Acid,  $C_{13}H_{26}O_2$ .**

Tridecanoic acid is said to be present in small percentages in the oil of iris. It is a crystalline solid with a faint, rather pleasant, odor. A simple laboratory synthesis consists of the hydrolysis of tridecanenitrile prepared from commercially available *n*-dodecyl bromide or chloride. Other methods of synthesis are the oxidation of methyl *n*-tridecyl ketone with potassium dichromate and sulfuric acid; the oxidation of 2-hydroxymyristic acid (from  $\alpha$ -bromomyristic acid) (2); the oxidation of 1-tridecanol; and the malonic acid synthesis from *n*-undecyl iodide (3). Tridecanoic acid is one of the oxidation products of paraffin (1). The acid is of research interest only.

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M. G. GERGEL AND MAX REVELISE

**Myristic Acid,  $C_{14}H_{28}O_2$ .**

Myristic acid is present in almost all vegetable and animal fats. In most of these it is found in relatively small amounts, although milk fat contains about 10% and palm-seed fats contain 15-20% of the acid. Myristic acid is the major constituent of the seed fat of nutmeg and related species and comprises 70-80% of the fatty acids of nutmeg butter. Myristic acid is an odorless crystalline solid with a somewhat waxy feel.

A fractionally distilled myristic acid of 90% purity is commercially available. This commercially pure myristic acid is less available than lauric acid and is accordingly somewhat higher priced. During the ten-year period 1939-49, the price ranged between 30 and 50¢/lb. In general, myristic acid finds similar application to lauric acid, particularly where either slightly lower solubility or slightly higher melting point is desirable. In addition, myristic acid is used in shaving creams, shampoos, cosmetics, and in compounding rubber, paints, and greases. On reduction it yields myristyl alcohol (see Vol. 1, p. 319). See also "Manufacture from fats," p. 231.

H. J. HARWOOD AND E. F. BINKERD

**Pentadecanoic Acid,  $C_{15}H_{30}O_2$ .**

Pentadecanoic acid has not been found in natural fats and oils but may be synthesized by methods similar to those employed for the preparation of tridecanoic acid. The synthetic acid is an odorless crystalline solid with a somewhat waxy texture. Pentadecanoic acid can be prepared inexpensively from the 2-hydroxy derivative of palmitic acid, or by passing from the commercially available myristyl alcohol (1-tetradecanol) through the bromide to the nitrile, followed by hydrolysis. The acid is of research interest only.

M. G. GERGEL AND MAX REVELISE

**Palmitic Acid,  $C_{16}H_{32}O_2$ .**

Palmitic acid is the most abundant naturally occurring saturated fatty acid and is found in practically all vegetable and land- and marine-animal fats. It is a major constituent of lard, tallow, cocoa butter, and most fruit-coat fats. Of the latter, palm oil contains 35-40% palmitic acid and Chinese vegetable tallow almost 70%. Palmitic acid is an odorless waxy solid.

After "splitting" of a fat or oil (see p. 231), commercial palmitic acid is separated from the fatty acid mixtures by two different processes. Since unsaturated fatty acids of the same chain length occur in significant amounts only in marine oils, it is possible to separate palmitic acid by fractional distillation of the fatty acids from other fats. The other important process for the production of palmitic acid involves the fractional crystallization of fatty acid mixtures from a solvent such as acetone or methanol. By selection of a fatty acid mixture, such as that derived from palm oil, which is relatively low in stearic acid and high in palmitic and unsaturated acids, the saturated acids are readily separated from the unsaturated acids, yielding a "high-palmitic acid" fraction. Fractionally distilled palmitic acid is of 90% purity. The price, which ranged between 15 and 30¢/lb. during the period 1939-49, fluctuates with the price of fats. The price quoted in June 1950 was 14¾¢/lb. for carload lots.

As with lauric and stearic acids, the important derivatives are the esters, metallic salts, cetyl (or palmityl) alcohol (see Vol. 1, p. 320), amides, nitriles, amines, and quaternary ammonium salts (see p. 221).

The largest use of palmitic acid is as the mixture found in commercial stearic acid, of which it constitutes 55%. Commercially pure palmitic acid or its derivatives find use in a wide variety of applications where the properties of the alkyl chain containing sixteen carbon atoms are most suitable. The more important uses of the acid or its derivatives are in paints and other coatings, greases, cosmetics, plastics, soaps, and synthetic detergents.

H. J. HARWOOD AND E. F. BINKERD

### Margaric Acid, $C_{17}H_{34}O_2$ .

Margaric acid has not been found in natural fats and oils. Substances isolated from natural oils and thought to be margaric acid have proved to be mixtures of palmitic and stearic acids (5,9). Synthetic margaric acid is a waxy crystalline solid. *n*-Hexadecyl (cetyl) bromide or chloride, both available commercially, may be used for the synthesis of the pure acid by conversion to the nitrile, followed by hydrolysis. Other methods of preparation include: the reaction of *n*-hexadecylmagnesium iodide with carbon dioxide (7); and the reaction of silver stearate and iodine with subsequent saponification to yield 1-heptadecanol, followed by oxidation (1).

Considerable clinical research has been expended upon the application of the glyceride of margaric acid (intarvin) in the treatment of diabetes mellitus, on the assumption that the end products of the metabolism of odd-carbon glycerides cannot be ketone bodies. Available reports differ sharply, and the subject seems to merit additional study (2,3,4,6,8).

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M. G. GERGEL AND MAX REVELISE

### Stearic Acid, $C_{18}H_{36}O_2$ .

Stearic acid is the highest saturated fatty acid prominent in naturally occurring fats and oils (3,9). It is a major constituent of animal fats (20-30%) and of certain vegetable fats such as cocoa butter (34%). Stearic acid is a waxy solid.

The manufacture of stearic acid is accomplished by one of several processes depending upon the starting material and the quality of product desired. In every case the first step in the process is one of fat "splitting" or hydrolysis (see p. 231). Where high stearic acid content is desired, it is customary to hydrogenate an oil that is low in

palmitic acid and high in oleic and linoleic acids; thus, the fatty acids of completely hydrogenated soybean or corn oil contain over 90% stearic acid. Commercially pure stearic acid is produced by fractional distillation of saturated fatty acid mixtures and is being offered in purities exceeding 95%. Since it is not possible to separate saturated from unsaturated fatty acids of the same chain length by distillation, this separation is accomplished by crystallization processes either with or without solvent.

The most important saturated fatty acid in commerce today is "commercial stearic acid." Actually, this is a mixture consisting of approximately 55% palmitic acid and 45% stearic acid. This product may be produced by solvent crystallization, but the majority is obtained by the process of crystallization without solvent termed "panning and pressing." In this manner, there are produced three grades of stearic acid: single-, double-, and triple-pressed, which vary in their oleic acid content. Triple-pressed stearic acid, the best grade, contains about 3% oleic acid and has a titer (melting point) of 55.0–55.5°C.

The ratio of stearic to palmitic acid in commercial stearic acid is the ratio normally found in tallow. Although this mixture has been a commodity for many years, there is a growing demand for other mixtures in which the ratio of acids is varied to meet specific demands. This variation is best achieved by fractional distillation, solvent crystallization, or a combination of the two.

The price of stearic acid fluctuated between 15 and 25¢/lb. during the decade 1939–49. In June 1950, the price of single-pressed stearic acid was 13–13¾¢/lb., double-pressed was 14¢/lb., and triple-pressed was 16¼–16¾¢/lb. Production of stearic acid in the U.S. in 1948 amounted to 66,363,000 lb. Approximately 40% of the stearic acid produced is used in the production of rubber. Appreciable amounts (3–8% in each case) of stearic acid are used in the fields of metalworking, protective coatings, resins, textile treating, pharmaceuticals, toilet articles, and candles.

Although stearic acid finds application as the free acid in some uses, as for example in candles, and in rubber and metalworking and finishing, it is used mainly in the form of salts, esters, and other derivatives (see *Driers and metallic soaps*; *Esters, organic*). Stearoyl chloride, prepared by the chlorination of stearic acid with phosphorus trichloride, thionyl chloride, or phosgene, is used as an intermediate in the formation of esters and amides. The more important nitrogen derivatives of stearic acid, stearamide and stearonitrile, are manufactured by treating the fatty acid with ammonia (see p. 221).

**Stearyl alcohol** (1-octadecanol, *n*-octadecyl alcohol),  $\text{CH}_3(\text{CH}_2)_{17}\text{OH}$ , formula weight 270.49, is a waxlike substance; m.p. 58.5°C.;  $b_{15}$  210.5°C.;  $d_4^{50}$  0.8124. Its natural source is the sperm and blubber oil of the whale, porpoise, and dolphin. It has also been found in the oil of herring and in the caudal glands of the goose. Its isolation from the coelenterate (gorgonias) *Plexaura flexuosa* and from the pollen fat of *Ambrosia artemisifolia* L. has also been reported. It has also been isolated from the hydrogenation product of the dioxane-insoluble fraction of artificial cellulose coal (2).

Stearyl alcohol can be prepared from stearic acid or its methyl, ethyl, or butyl ester, by reduction with hydrogen in the presence of cobalt (16), copper chromite (11,17), or nickel (13), or with lithium aluminum hydride (12), or sodium and butyl alcohol (1). Stearyl alcohol can also be prepared from butyl oleate with copper oxide–chromium oxide catalyst (15), and from sodium stearate and calcium formate in cyclohexane with copper catalysts (10). Stearyl alcohol, usually in combination with other fatty alcohols, is produced by the reduction of sperm oil and hydrogenated cottonseed, corn, and sun-

flower oils (6,7). Stearyl alcohol (U.S.P. XIV) is available in 50-lb. fiber drums, and the technical grade (Stenol Fatty Alcohol) in 50-lb. paper bags.

Stearyl alcohol, like cetyl alcohol (see Vol. 1, p. 320), is used as an ingredient in ointment bases (8), cosmetic creams (4,10), lotions, etc. Official preparations that include stearyl alcohol are hydrophilic ointment and hydrophilic petrolatum (U.S.P. XIV), and N.F. sun cream (N.F. IX). It is also used as an emulsifier (5), finishing agent, antifoam agent, lubricant additive, and in rubber processing. Phosphated stearyl alcohol is used as a suppository base (14). Its esters with organic acids have many and varied medicinal and industrial uses.

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H. J. HARWOOD AND E. F. BINKERD  
MABEL D. REINER (Stearyl Alcohol)

### Nonadecanoic Acid, $C_{19}H_{38}O_2$ .

Nonadecanoic acid has not been found in natural fats, oils, or waxes, but has been prepared synthetically. The acid is a waxy crystalline solid. Nonadecanoic acid can be prepared easily from *n*-octadecyl bromide or iodide by the nitrile method or by one of the reactions indicated for the synthesis of pentadecanoic or margaric acid. Nonadecanoic acid is of research interest only.

M. G. GERGEL AND MAX REVELISE

### $C_{20}$ - $C_{35}$ Saturated Acids.

**Arachidic acid**,  $C_{20}H_{40}O_2$ , is widely distributed in nature. It is a major constituent of rambutan tallow (20-35%), pulasan tallow (22.3%), macassar-nut fat (22.6%), and kusum (over 20%). Of the vegetable oils, peanut contains from 3-4%, poke root about 6%, and coffee bean over 2%. However, it is generally a minor component in most fats and oils. The following vegetable oils contain less than 1%: cottonseed, sunflower, rubber, radish, melon, ben (behen), and mango seeds, soybean, corn, rice, olive, palm, rape, and cocoa butter. It is also reported to be present in carnauba wax and in the wax of pine bark. It is found in small amounts in animal

depot fats such as sheep, lion, and tiger fat, and in cow's, mare's, goat's, ewe's, and human milk. Arachidic acid has been extracted from the fat of human hair and wool and also from the fats of insects and yeasts. (*Isoarachidic acid* (methylnonadecanoic acid) also has been reported to occur in wool fat.) The presence of arachidic acid in the oils of sardines, whales, and shark liver is also reported. Appreciable amounts have been obtained from hydrogenated fish oils. It has been isolated from a petroleum distillate.

One of the most satisfactory procedures for the synthesis of arachidic acid is the hydrolysis of eicosanenitrile. It has also been prepared by the oxidation of a high-molecular synthetic paraffin.

Arachidic acid is mainly of research interest.

**Heneicosanoic acid**,  $C_{21}H_{42}O_2$ , has been reported to occur in Japanese wax and earth-nut oil, but the evidence presented indicates that it is not found in natural fats and waxes. It can be prepared from arachidic acid by the nitrile method or by the oxidation of methyl *n*-heneicosyl ketone.

**Behenic acid**,  $C_{22}H_{44}O_2$ , occurs to the extent of 17% in the oil of the seeds of *Xylia xylocarpa* (7) and 14.2% in the oil of the nut of *Lophira alata*, a tree indigenous to Africa (4). More generally, this acid occurs as a minor component in the fats of seeds such as ben (behen), radish, mustard, rape, rice bran, and peanut. It is also found in nim blossoms (8), in the leaves of *Didymocarpus pedicellata* (17), in carnauba wax, in montan wax, and in the wax of various pines. The fat of human hair contains 2% (19) and the mycelium of *Phycomyces blakesleeana*, 1.7% (1). Behenic acid is present in small amounts in human milk fat, butterfats, and marine oils such as sardine, whale, and shark-liver oils. Large amounts are found in the following hydrogenated oils: jamba, 50.8%; mustard-seed, 46.3%; rape, 57.6%; herring, 7%; sardine, 18%; and cod-liver, 13%.

Behenic acid is easily prepared by the reduction of normal unsaturated acids having 22 carbon atoms or of their halogen substitution products.

**Tricosanoic acid**,  $C_{23}H_{46}O_2$ , does not occur in natural sources, though its presence in peanut oil and in the wax of olive leaves has been reported. It is prepared by the reduction of 13-ketotricosanoic acid, which can be obtained by condensing the sodium derivative of ethyl 2-acetylbrassylate with stearoyl chloride.

**Lignoceric acid**,  $C_{24}H_{48}O_2$ , is present in many oils, fats, and waxes. It has been found, usually in small amounts, in the following seed oils: corn, 0.2%; soybean, 0.1%; sesame, 0.04%; black walnut, 0.04%; sunflower, 0.4%; rape, 0.8–2.4%; mustard, 1.1%; coffee bean, 1.8%; ben (behen), 5.3%; and peanut oils. Larger amounts have been reported in the oil of the seeds of ringworm shrub, which contains 14.96% (14), and of the deciduous tree *Adenanthera pavonina*, which contains 25.5%. Lignoceric acid has been reported to have been obtained from the latter source in a yield of 1.5% based on the weight of the seeds. It is also present in the wax of the flowers and the oil of the seeds of *Butea frondosa* (9) and in the leaves of *Didymocarpus pedicellata* (17). About 12% of the total fatty acids of the oil from pines is lignoceric acid (11). It has been isolated from the oil of the bark of pine (10) and from the oil of the heartwood of Douglas fir (3). The marine oils contain small amounts of lignoceric acid. It is found in larger amounts in hydrogenated fish oils; hydrogenated sardine oil contains 4.0% and hydrogenated herring oil, 6.0%. It has also been obtained from the hydrogenation product of the lignin residue of Douglas fir (2). The presence of lignoceric acid in the following animal fats has been reported: wool fat (18); butterfat;



sphingomyelin and cerebrosides of milk (about 80% of the fat constituents) (6); sphingomyelin from ox spleen (15); and kidney fat.

The fat of the mold *Aspergillus niger* contains 11.8%, and of the mycelium of *Phycomyces blakesleeanus*, 2.1% (1). Its presence in the organic matter of Formosa soil has also been reported (16).

The insect waxes such as Chinese wax and beeswax, the mineral waxes such as montan wax, the plant waxes such as carnauba (5) and that from the seeds of "nurude" (13), and the bacterial waxes contain lignoceric acid.

The acid can be synthesized by a number of methods, the hydrolysis of tetracosanenitrile giving almost quantitative yields. It is also formed by the distillation of rotten oak wood.

**Pentacosanoic acid**,  $C_{25}H_{50}O_2$ , has not been found in naturally occurring fats and waxes. It has been prepared by the conversion of lignoceric acid to pentacosanenitrile followed by hydrolysis.

**Cerotic acid**,  $C_{26}H_{52}O_2$ , has been found in practically every wax examined. It occurs principally as esters of the higher fatty alcohols. The presence of cerotic acid in the following waxes has been reported: Gedda, wool, montan, cotton, bamboo, carnauba, flax, and floral waxes. It can be obtained from the wax of stick lac, Chinese wax, and beeswax. Although only traces have been found in the vegetable fats such as peanut and pumpkin-seed oils, and the fats of spinach and rice polishings, appreciable amounts have been isolated from the fat of fern spores. It is also present in the oils from the leaves of *Globularia alypum* and from the mycelium of *Phycomyces blakesleeanus*. Cerotic acid can be prepared from Chinese wax, beeswax, or montan wax by saponification and the fractionation of their mixed acids.

**Heptacosanoic acid**,  $C_{27}H_{54}O_2$ , probably does not occur in natural products. It can be synthesized by preparing the nitrile from 1-hexacosanol and hydrolyzing it.

**Montanic acid**,  $C_{28}H_{56}O_2$ , has been reported to occur almost exclusively in the vegetable, insect, and mineral waxes. It has been found in most of the waxes that have been investigated. Montan wax has been found to contain 41.33%. This acid has also been isolated from beeswax, Chinese wax, cotton wax, carnauba wax, candle-lilla, and from some of the lignite waxes of peat. Octacosanoic acid can be synthesized by a number of methods but it is most generally prepared by isolation from natural sources. The condensation product of montanic acid with aliphatic primary or secondary amines can be used as a shoe cream, floor polish, etc. (20).

**Nonacosanoic acid**,  $C_{29}H_{58}O_2$ , has been reported to occur in Bohemian montan wax and in a bitumen wax of peat. It has been synthesized from montanic acid by the nitrile method.

**Melissic acid**,  $C_{30}H_{60}O_2$ , is found almost exclusively in waxes. It is present in the insect waxes—beeswax, Chinese wax, coccid waxes, and the waxes of cocoon fibers, and of the scale insect *Ceroplastes rubens*. Melissic acid also occurs in sugar cane, elematis, bayberry, cotton, carnauba, and slash-pine waxes. Its presence in the bitumen waxes such as montan wax has also been reported. Only traces of melissic acid have been found in palm oil. It can be prepared by the oxidation of myricyl (melissyl) alcohol,  $C_{30}H_{61}OH$ .

**Hentriacontanoic acid**,  $C_{31}H_{62}O_2$ , has been reported to be present in several waxes, but it is probable that the product investigated was a mixture of even-numbered acids. Hentriacontanoic acid has been synthesized by oxidation of 1-triacontanol followed by hydrolysis of the resulting hentriacontanenitrile.

**Dotriacontanoic acid**,  $C_{32}H_{64}O_2$ , which has also been called lacceroic acid, has been obtained from the wax of stick lac. Methods for its synthesis are: oxidation of 1-dotriacontanol; malonic acid synthesis from 1-iodotriacontane; and the reaction of *n*-docosylzinc iodide with the half-ester half-acid chloride of sebacic acid, reduction of the keto acid to the hydroxy acid, replacement of the hydroxyl group with iodine, and removal of the latter with zinc dust in glacial acetic acid (12).

**Tritriacontanoic acid**,  $C_{33}H_{66}O_2$ , has been reported to be the psylic acid or ceromelissic acid isolated from the waxes of *Ceroplastes ceriferus* and from the scale insect *Ceroplastes rubens*, but its presence in natural sources is doubtful.

**Tettratriacontanoic acid**,  $C_{34}H_{68}O_2$ , has been obtained from Gedda wax and has been called geddic acid. It can be prepared by the oxidation of 1-tettratriacontanol, by the Clemmensen reduction of 13-ketotettratriacontanoic acid and from dotriacontanoic acid by the malonic ester synthesis.

**Pentatriacontanoic acid**,  $C_{35}H_{70}O_2$ , has been reported in olive wax and in the wax of *Ceroplastes rubens*, and has also been called ceroplastic acid. It has been synthesized from 1-tettratriacontanol by the nitrile method.

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MABEL D. REINER

#### BRANCHED-CHAIN SATURATED ACIDS

The branched-chain fatty acids contain one or more branching alkyl groups. Not considered here are the aryl-substituted fatty acids, whose physical and chemical properties are very different from those of the other fatty acids, or the naphthenic acids (*q.v.*), which contain an alicyclic ring in close proximity to the carboxyl group. For other alicyclic-substituted acids, whose properties are more like those of the branched-chain acids, see "Chaulmoogra-oil acids," p. 295. While a number of branched-chain fatty acids occur in various sources, only isovaleric acid occurs in large amounts.

**$\alpha$ -Methylbutyric Acid,  $C_5H_{10}O_2$ .**

$\alpha$ -Methylbutyric acid (methylethylacetic acid) is the only valeric acid isomer that exists in optically active forms, and is therefore often called active valeric acid.  $\alpha$ -Methylbutyric acid has been isolated from the oil of *Angelica archangelica* roots (2). The dextrorotatory form (*dextro*-valeric acid),  $[\alpha]_D^{21} + 17.6^\circ$ , has been found in lavender oil (3) and in clinical penicillin (1), and the levorotatory form (*levo*-valeric acid) in champaca-flower oil. *dl*- $\alpha$ -Methylbutyric acid can be prepared by heating methylethylmalonic acid, and also by treatment of tetrahydrofuran with carbon monoxide at 740–800 atm., in the presence of a nickel carbonyl catalyst (4). *dextro*-Valeric acid can be prepared by oxidation of *levo*-amyl alcohol ("d-amyl alcohol," *levo*-2-methyl-1-butanol) with potassium dichromate and sulfuric acid.

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**Isovaleric Acid,  $C_5H_{10}O_2$ .**

Large quantities of isovaleric acid occur in the free state in valerian root. It is also found in the oils of the dolphin, porpoise jaw, pineapple, and lavender, and has been isolated from the distillation products of pilot-whale head oil, from raw cracked gasoline, and from the decomposition products of the acids extracted from gum gamboge resin (1).

Isovaleric acid is formed during the high-pressure synthesis of alcohols from carbon monoxide and hydrogen (4). The catalytic oxidation of isoamyl alcohol by carbon dioxide (2) and the electrolytic oxidation of isoamyl alcohol (3) yield isovaleric acid.

It is used as an intermediate in the preparation of various industrial compounds and medicinals. Its lead salt has been suggested for waterproofing films prepared from inorganic silicate or hydrous oxide,  $(SiO_2)_n \cdot (H_2O)_n$  (5).

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MABEL D. REINER

**Pivalic Acid,  $C_5H_{10}O_2$ .**

Pivalic acid (trimethylacetic acid) has not been reported to occur in natural products. It can be prepared by: (1) carboxylation of isobutylene with carbon monoxide in aqueous sulfuric acid (5); (2) oxidation of diisobutylene in the presence of potassium hydroxide (1); (3) reaction of acetone with carbon monoxide and steam in the presence of potassium hydroxide (2); (4) oxidation of pinacolone; and (5) reaction of *tert*-butylmagnesium halides with carbon dioxide (3).

Pivalic acid is useful for plasticizing zein compositions to form products having applications as impregnating agents, adhesives, and in printing inks (4). It is employed as an intermediate in the synthesis of products having various industrial uses and to prepare esters of some therapeutically active alcohols.

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MABEL D. REINER

### 2-Ethylhexanoic Acid, $C_8H_{16}O_2$ .

2-Ethylhexanoic acid (often called 2-ethylhexoic in industry) is a liquid having a mild odor: vapor pressure at 20°C., 0.03 mm. Hg; viscosity at 20°C., 7.73 centipoises; flash point (Cleveland open cup), 260°F.; coefficient of expansion at 20°C., 0.00089/°C. 2-Ethylhexoic acid is soluble in water to the extent of 0.25% by weight at 20°C.

2-Ethylhexoic acid can be made by the hydrogenation of 2-ethyl-2-hexenal ( $\alpha$ -ethyl- $\beta$ -propylacrolein),  $CH_3(CH_2)_2CH:C(C_2H_5)CHO$ , to 2-ethylhexanal ( $\alpha$ -ethylcaproaldehyde), which is catalytically oxidized in the liquid phase to the acid (13).

The metallic salts of ethylhexoic acid (known also as octoates) are used as varnish driers (see *Driers and metallic soaps*). The important salts are mainly those of lead, cobalt, and manganese, and are made by diffusion or double decomposition (1,2,4).

Other ethylhexoates find uses like those of metallic soaps of other acids. The basic lead salt and the barium salt are heat stabilizers for polyvinyl resins, and the salts of light metals such as aluminum are useful in greases and as thickening agents in certain lacquers and paints (6). Other ethylhexoates such as those of cobalt, nickel, zinc, and magnesium can be used to inhibit sludge deposition in mineral oils (7). Copper ethylhexoate has been suggested to replace copper naphthenate partially or wholly as a fungicide (10).

Certain derivatives of ethylhexoic acid are used as plasticizers (*q.v.*): polyethylene glycol bis(2-ethylhexoate) (Flexol plasticizer 4GO) for smooth vinyl films and sheeting (5), the diester amide of 2-ethylhexoic acid and diethanolamine (Flexol plasticizer 8N8) for vinyl resins (15), and the products from 2-ethylhexoic acid and various amino resins (12). 2-Ethylhexoic acid can also be used as a plasticizer for zein compositions employed for impregnating, coating, etc. (9). Its esters of polyoxyalkylenediols are used as metal lubricants (14), and the *N*-ethylhexoyl derivative of 3-amino-1-thia-cyclopentane 1,1-dioxide has been reported as an oil additive (11).

2-Ethylhexoic acid itself has been used as an insect repellent (8), and in the extraction of acetic acid from dilute aqueous solutions (3).

### Bibliography for 2-Ethylhexanoic Acid

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J. A. FIELD

### Higher Branched-Chain Acids.

The higher branched-chain fatty acids have been synthesized only by multistep processes and are of little, if any, real industrial significance. It is probable, however, that their presence in such products as heavy-metal soaps may affect the properties of these products.

#### OCCURRENCE

The occurrence of higher branched-chain acids in nature was first demonstrated in 1929 by Anderson (2), who isolated such acids from the lipides of acid-fast bacteria. Subsequent interest in branched-chain acids has arisen largely from this unusual occurrence in nature, especially since the tubercle bacillus was one of the organisms from which they were isolated. A review of the acids from bacteria has appeared (1). These acids were usually low-melting and in mixtures that were separated with difficulty. One relatively homogeneous material, termed phthioic acid and containing twenty-six carbon atoms, has been shown to give typical tubercular lesions on injection in experimental animals. Very little is known concerning the structure of this acid. The only branched-chain acid from bacteria whose structure has been definitely established is tuberculostearic acid, which is (-)-10-methyloctadecanoic acid (9).

An extensive series of branched-chain acids has been isolated from wool fat (*q.v.*) (dégiras) by Weitkamp (15). There was one series of *iso acids* (with branching methyl on the carbon second from the end of the chain), including all even-carbon acids from C<sub>10</sub> to C<sub>26</sub>, and one series of dextrorotatory *anteiso acids* (with branching methyl on the carbon third from the end of chain), including all odd-carbon acids from C<sub>9</sub> to C<sub>27</sub>. There was also present the series of normal even-carbon acids from C<sub>10</sub> to C<sub>26</sub>. This isolation is notable as the only example of the natural occurrence of high-molecular branched-chain or odd-carbon acids, except in bacteria. Since all the iso acids have melting points nearly the same as those of the normal acids, it seems possible that others may occur in nature, but have been overlooked.

Lower-molecular branched-chain acids (with seven or less carbons) have been isolated from petroleum (10), and higher ones probably occur but in mixtures that have not been separable. Thus far, there has been isolated no acid containing a branching group larger than methyl, but some have been prepared.

## PROPERTIES

No large amount of correlated data concerning physical properties of branched-chain acids has been accumulated, but a few properties may be mentioned.

*Melting Point.* The iso acids have melting points very close to those of the corresponding normal acids, while all other branched-chain acids have considerably lower melting points than those of the normal isomers. No other known type of high-molecular branched-chain acid has a melting point higher than 10°C. below that of the normal isomer. Numerous acids reported as having melting points in this region have later been shown to be mixtures of normal acids. As a branching group is moved from

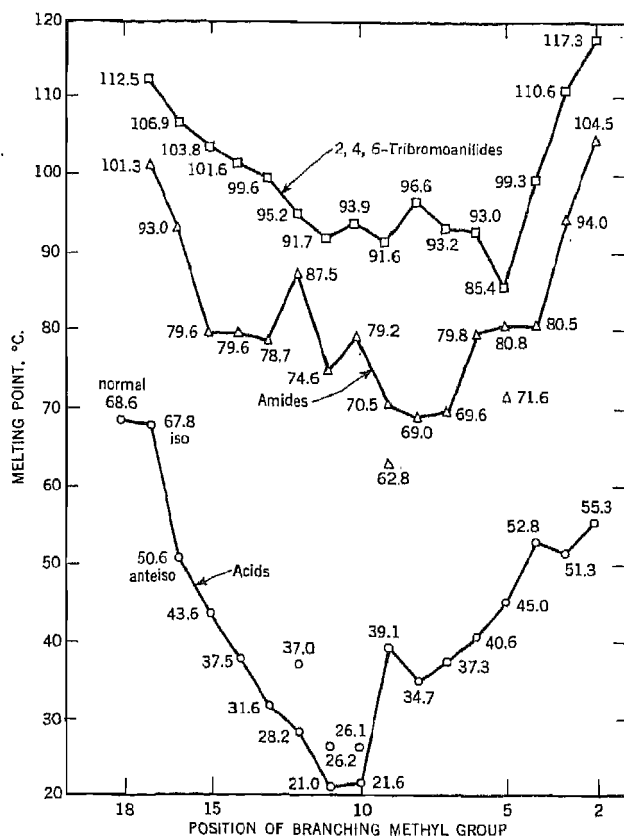


Fig. 1. Melting points of methyloctadecanoic acids and their derivatives (5).

either end of the chain toward the center, the melting point decreases in a fairly regular manner and reaches a minimum when the branching group is somewhere near the center of the chain. The entire series of monomethyloctadecanoic acids has been prepared, and the lowest-melting isomers are the 10- and 11-methyloctadecanoic acids (m.p. 21.6°C. and 21.0°, respectively, for the lower-melting polymorphs). The amides of these acids show no such regular variation of melting point with position of the branching methyl group, and many of these isomeric amides have nearly the same melting points. The tribromoanilides, however, present a more regular pattern than the amides and are more satisfactory derivatives for investigation. The melting points of the methyloctadecanoic acids and their derivatives are shown in Figure 1, but the

various polymorphic forms of the amides and tribromoanilides are omitted for the sake of clarity. These are described in the original reference (5).

Table I gives melting points for various types of branched-chain acids, grouped according to type. Table II gives data for the dextro forms of some optically active

TABLE I. Optically Inactive Branched-Chain Acids and Derivatives.

Acid	Formula	M.p., °C.			
		Acid	Amide	2,4,6-Tribromoanilide	p-Bromoanilide
14-Ethylhexadecanoic	$\text{CH}_3\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)(\text{CH}_2)_{12}\text{COOH}$	42.9	79.9	101.0	—
15-Ethylheptadecanoic	$\text{CH}_3\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)(\text{CH}_2)_{13}\text{COOH}$	37.4	81.1	102.2	—
20-Ethyltricosanoic	$\text{CH}_3\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)(\text{CH}_2)_{18}\text{COOH}$	65.5	90.6	105.3	—
18-n-Propylheicosanoic	$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{C}_3\text{H}_7)(\text{CH}_2)_{10}\text{COOH}$	52.2	82.4	93.6	—
2-Methyltetracosanoic	$\text{CH}_3(\text{CH}_2)_{21}\text{CH}(\text{CH}_3)\text{COOH}$	72.5	111.5	—	—
6-Methyltetracosanoic	$\text{CH}_3(\text{CH}_2)_{17}\text{CH}(\text{CH}_3)(\text{CH}_2)_6\text{COOH}$	56.6	85.3	97.2	—
10-Methyltetracosanoic	$\text{CH}_3(\text{CH}_2)_{13}\text{CH}(\text{CH}_3)(\text{CH}_2)_8\text{COOH}$	51.5	78.5	84.8	—
14-Methyltetracosanoic	$\text{CH}_3(\text{CH}_2)_9\text{CH}(\text{CH}_3)(\text{CH}_2)_{12}\text{COOH}$	58.5	81.0	87.5	—
18-Methyltetracosanoic	$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{CH}_3)(\text{CH}_2)_{16}\text{COOH}$	55.8	87.5	—	82.5
12-n-Hexyloctadecanoic	$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{C}_6\text{H}_{13})(\text{CH}_2)_{10}\text{COOH}$	28.7	—	—	67.8
9-n-Octylheptadecanoic <sup>a</sup>	$\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{C}_8\text{H}_{17})(\text{CH}_2)_7\text{COOH}$	14	—	—	80.1
2-n-Butyl-2-ethylnonanoic <sup>c</sup>	$\text{CH}_3(\text{CH}_2)_6\text{C}(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)\text{COOH}$	—	—	—	89.0
4-n-Butyl-4-ethylnonanoic <sup>b</sup>	$\text{CH}_3(\text{CH}_2)_4\text{C}(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)\text{CH}_2\text{CH}_2\text{COOH}$	—	—	—	122.2
2,2-Dimethyloctadecanoic	$\text{CH}_3(\text{CH}_2)_{15}\text{C}(\text{CH}_3)_2\text{COOH}$	58.0	86.0	—	85.4
3,3-Dimethyloctadecanoic	$\text{CH}_3(\text{CH}_2)_{14}\text{C}(\text{CH}_3)_2\text{CH}_2\text{COOH}$	44.8	58.5	—	89.7

<sup>a</sup>  $n_D^{20}$  1.4585. <sup>b</sup>  $n_D^{27}$  1.4533. <sup>c</sup>  $n_D^{27}$  1.4472.

TABLE II. Optically Active Branched-Chain Acids and Derivatives.

Acid	Formula	[M] <sub>D</sub> , degrees	M.p., °C.	
			Acid	Amide
2-Methyldodecanoic	$\text{CH}_3(\text{CH}_2)_9\text{CH}(\text{CH}_3)\text{COOH}$	+28.3	22.0	93.8
2-Methylhexacosanoic	$\text{CH}_3(\text{CH}_2)_{23}\text{CH}(\text{CH}_3)\text{COOH}$	+28.0	69.9	115.6
3-Methyloctadecanoic	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}(\text{CH}_3)\text{CH}_2\text{COOH}$	+14.5	44.1	91.7
3-Methyltetracosanoic	$\text{CH}_3(\text{CH}_2)_{20}\text{CH}(\text{CH}_3)\text{CH}_2\text{COOH}$	+13.2	65.6	102.3
3-Methylheptacosanoic	$\text{CH}_3(\text{CH}_2)_{23}\text{CH}(\text{CH}_3)\text{CH}_2\text{COOH}$	+13.5	73.1	105.4
10-Methyloctadecanoic	$\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{CH}_3)(\text{CH}_2)_8\text{COOH}$	+0.2	13.5	76.4
12-Methyltetradecanoic	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_{10}\text{COOH}$	+11.4	23.0	86.4
2,9-Dimethyloctadecanoic	$\text{CH}_3(\text{CH}_2)_8\text{CH}(\text{CH}_3)(\text{CH}_2)_6\text{CH}(\text{CH}_3)\text{COOH}$	+30.0	34.8	90.8





what different chain extension (12), depending on acylation of a  $\beta$ -keto ester with an ester acid chloride. The chain may be readily extended by as many as ten carbons in one operation, for the ten-carbon dibasic acid sebacic acid is commercially available.

#### DETERMINATION OF STRUCTURE

Location of branching groups in a branched-chain acid has been difficult, but has been studied to a considerable extent in an effort to learn the structures of the acids from bacteria. Oxidation with chromic acid, infrared spectroscopy, and x-ray diffraction have been applied in some instances, but these methods have been somewhat limited in their applications. Methyl groups in the  $\alpha$ - or  $\beta$ -position may be located by a study of the rate of amide hydrolysis (6), and Weitkamp's method of studying phase diagrams of branched- and straight-chain acids has been useful for locating methyl groups near the end of the chain. General methods for locating groups near the middle of the chain have not been reported, but the problem is being investigated in several laboratories. The extension of Weitkamp's work to acids with branching methyl groups in various positions along the chain appears promising, but the scope and limitations of the method are yet to be established (5).

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JAMES CASON

#### UNSATURATED ACIDS

##### 10-Undecylenic Acid, $C_{11}H_{20}O_2$ .

10-Undecylenic acid, formula weight 184.28, is a low-melting crystalline solid. It does not occur naturally, but is formed by the pyrolysis of ricinoleic acid and its derivatives, and is one of the products obtained by the vacuum distillation of castor oil. The decomposition products formed during the dehydration of castor oil (see Vol. 3, pp. 241-43) contain appreciable quantities of undecylenic acid and constitute a commercial source of the acid. In the laboratory, 10-undecylenic acid may be prepared by the malonic acid synthesis (1). The total reported U.S. production of undecylenic acid in 1947 was 91,000 lb.

The sterilizing action of the acid and its salts is remarkable, the action of the un-

saturated acids being generally stronger than that of saturated acids at the same concentration (4). The sodium salt is most fungistatic for common pathogens (3). The zinc salt is incorporated in a popular remedy for fungoid infections such as athlete's foot. The amides, especially the isobutylamide, have shown promise as insecticides against house flies and body lice (5). Undecylenic acid is a good starting point for the synthesis of ketonic perfumes (2). The alcohol derived from hydrogenation of ethyl or butyl undecylenate is itself a perfume ingredient.

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M. G. GERGEL AND MAX REVELISE

### Petroselinic Acid and Petroselaidic Acid, $C_{18}H_{34}O_2$ .

Petroselinic acid (*cis*-6-octadecenoic acid), formula weight 282.46, is a white solid, which was first isolated from parsley-seed oil and subsequently from ivy-seed, carrot-seed, celery-seed, and coriander-seed oils. This acid is a major component of the seed fats of the *Araliaceae* and *Umbelliferae*. Petroselinic acid, when heated with nitrous acid or selenium, is isomerized to petroselaidic acid, which has been shown by its infrared absorption to have the *trans* configuration. Neither of these acids is a commercial product.

JOHN T. SCANLAN

### Oleic Acid, $C_{18}H_{34}O_2$ .

Oleic acid (*cis*-9-octadecenoic acid), formula weight 282.46, is probably the most abundant of the naturally occurring fatty acids. In the form of glycerides, it is found in substantial quantities in all land- and marine-animal fats and in all vegetable oils. In animal depot fats, it is the principal constituent, amounting to about 40 or 50% of the fat, but it occurs in the highest percentages in the vegetable oils, for example, olive oil, 70-85%, and almond oil, 75% or more. Approximately the following proportions are also found: peanut oil, 57%; corn oil, 45%; palm oil, 41%; squash-seed oil, 37%; cottonseed oil, 35%; soybean oil, 33%; and sunflowerseed oil, 33%. Two crystalline forms of oleic acid, m.p. 13.4 and 16.3°C., have been reported.

### REACTIONS

As the best-known, typical monounsaturated acid, oleic acid has been much studied. It undergoes the expected reactions of both the carboxyl group and an olefinic chain (see p. 208). It can be readily isomerized to the *trans* form, called elaidic acid (see p. 271).

Oleic acid can be oxidized to 9,10-dihydroxystearic acid by alkaline permanganate or by peracids, and to 9-hydroxy-10-keto- and 10-hydroxy-9-ketostearic acids by permanganate in neutral solutions. On cleavage under various conditions, it yields

azelaic acid, pelargonic acid, and the corresponding aldehydes, among other products (see pp. 212, 214). The production of di- and monobasic acids by oxidation of oleic acid with nitric acid in the presence of ammonium vanadate and similar oxidations with sodium hypochlorite in the presence of nickel salts have been patented but apparently not used commercially. The one process that has been used industrially and gives impure dibasic and monobasic acid fractions involves oxidation of red oil with chromic acid from spent tanning liquors. The process best suited for industrial production of short-chain mono- and dibasic acids from the monounsaturated acids, namely, catalytic air oxidation, has not as yet been developed commercially but it has been shown in the laboratory to give, under proper conditions, good yields of mixed scission products.

The reaction of sulfuric acid with oleic acid at low temperature, followed by hydrolysis of the ester formed, does not result, as might be supposed, in a mixture of the 9- and 10-monohydroxystearic acids. The double bond migrates in both directions along the carbon chain and the product is a mixture of many monohydroxy derivatives. The addition of chlorosulfonic acid proceeds in the same way as that of concentrated sulfuric acid.

In the presence of aluminum chloride (Friedel-Crafts synthesis), aryl groups can be added to the double bond of oleic acid. Such derivatives as phenyl-, xylyl-, tolyl-, phenoxyphenyl-, chlorophenyl-, and bromophenylstearic acids have been produced. Their sulfonated derivatives have surface-active properties. Because these products do not solidify at low temperatures, they have some promise as additives for lubricants intended for use in cold climates. Their salts with heavy metals have value in the prevention of metal corrosion.

#### ISOLATION OF PURE OLEIC ACID

It is very difficult to isolate oleic acid in the pure state from most of the fats in which it is found. The separation cannot be accomplished by distillation alone because its boiling point is too close to those of the accompanying  $C_{18}$  acids, stearic, linoleic, and linolenic. Even the  $C_{16}$  palmitic acid cannot be separated cleanly from oleic acid by the most efficient fractionating column. The methyl esters of these acids, however, can be fractionated by distillation under reduced pressure more readily than the acids.

For purification by solvent crystallization, on the other hand, the acids are preferable to the esters. Here again the accompanying acids interfere. Linoleic acid tends to solubilize oleic and the latter solubilizes the saturated acids, especially palmitic. The best starting material is therefore a fat in which the ratio of oleic to linoleic is greater than 5:1.

Olive oil, since it usually contains 80–85% oleic, 4–7% linoleic, and 7–10% palmitic acids, is the best material for laboratory preparations of pure oleic acid, though too costly for commercial production. The oil is saponified with alcoholic potassium hydroxide and the fatty acids are precipitated by acidification, dried, and fractionally distilled at about 4 mm. Hg. The distillate is twice crystallized from acetone at  $-55$  to  $-60^{\circ}\text{C}$ ., redissolved at room temperature, and cooled to  $-20^{\circ}\text{C}$ . The precipitate that forms is rejected and the acids from the filtrate are fractionally distilled as such or after conversion to methyl esters. In either case, the purity of the product (acid,  $b_d$  204–206 $^{\circ}\text{C}$ .; ester,  $b_d$  183–186 $^{\circ}\text{C}$ .) is about 96–99% (3).

## COMMERCIAL PRODUCTION

Commercial-grade oleic acid, commonly called "red oil," is usually made from inedible tallow (titer above 40°C.) or grease (titer below 40°C.) (2). Inedible tallow, rendered from butcher-shop trimmings, waste fats from small packing establishments, and fat from condemned and fallen animals, usually includes some pork fat and has a higher linoleic acid content than true beef tallow.

In the older process, the fatty acids obtained by acid hydrolysis (Twitchell process) of the fats (see p. 232) are subjected to one or more straight-run vacuum distillations. The distillate, consisting of about 40–50% saturated acids, mainly palmitic and stearic, as much as 10% linoleic acid, and about 40–45% of the monounsaturated oleic acid, is run into shallow pans and cooled slowly to about 40°F. in a refrigerated room. The cakes thus formed are wrapped in suitable cloth mats and subjected to moderate pressure in a hydraulic press. The expressed liquid is red oil and the residual solid is "single-pressed stearic acid."

Commercial-grade oleic acid (red oil) produced by this process varies in color from light yellow to deep red or brown. At its best, it seldom contains more than 75% oleic acid and the balance consists of about equal parts of linoleic acid and the saturated acids palmitic and stearic. Because of this fortuitous balance of impurities, the iodine number is usually very close to the theoretical value for pure oleic acid. Red oil is sold in various grades, based mainly on color and odor. Since the chemical composition varies little between grades, their resistance to oxidation is about the same. In some applications the oxidative deterioration has very undesirable results. Spontaneous combustion can occur in fibers that have been treated with red oil as a result of the heat generated by rapid autoxidation of the polyunsaturated acids present. When autoxidation proceeds slowly, gummy polymers are formed, which are difficult to remove by scouring; also, disagreeable odors and dark color may develop. Stabilizers or antioxidants are sometimes added to retard this type of deterioration.

About 1945, solvent crystallization was put into commercial operation in place of pressing (1). The solvent is 85–90% aqueous methanol, from which the saturated acids are precipitated and filtered off at low temperature. The process is continuous, more efficient, and cheaper than pressing, but the compositions of the solid and liquid fractions are substantially the same as those obtained in the older process. The content of unsaturated acids in the solid fraction can, however, be lowered by further washing with fresh solvent.

*Improved Technical Grade of Oleic Acid.* A new process which gives a technical oleic acid much superior in every respect to the present red oil has recently been introduced commercially (4,5). The essential feature of this process is the elimination of the polyunsaturated acids (linoleic and linolenic) by selective hydrogenation, that is, catalytic hydrogenation carried out under conditions that favor the conversion of the di- and triunsaturated acids to monounsaturated acids without any appreciable conversion of oleic acid to stearic acid. Best results are obtained if the hydrogenation is stopped when the concentration of polyunsaturated acids is 1% or a little less. If the process is continued beyond this point, there is a marked acceleration in the rate of formation of isomeric (isooleic) acids.

The starting material may be the same grades of inedible tallow or grease used for production of red oil, or a better grade of tallow. The hydrogenation may be carried out before or after acid hydrolysis of the glycerides. After hydrogenation and then hydrolysis, the dried fatty acids are distilled to reduce the content of unsplit glycerides

to a minimum, and the saturated acids are precipitated from acetone at about  $-20^{\circ}\text{C}$ . This solid fraction is obtained in good yield and corresponds approximately to "double pressed stearic acid." Distillation of the solvent from the filtrate yields a residue containing more than 90% monounsaturated acids, 1-3% polyunsaturated acids, and the remainder saturated acids. Fractional distillation at reduced pressure (4-5 mm. Hg) raises the oleic acid to as high as 98%. When the hydrogenation step is applied after hydrolysis, the mixture of fatty acids is first separated into a saturated and an unsaturated fraction by solvent crystallization as described above. The linoleic acid is then eliminated by selective hydrogenation of the unsaturated fraction, followed by purification of the oleic acid by solvent crystallization and vacuum fractionation. If hydrogenation is applied to the glycerides, both fatty acid fractions differ from the "stearic" and "oleic" acids obtained by the older processes because they contain isomers of oleic acid produced by hydrogenation of the polyunsaturated acids and isomerization of the oleic acid originally present. If the hydrogenation is applied to the free acids after hydrolysis and removal of the saturated acids, only the oleic acid fraction will contain these isomers.

Because of the low content of polyunsaturated acids, the oleic acid from this process is free from the more serious disadvantages from which crude red oil suffers. The elimination of the more highly unsaturated constituents, however, gives a product that solidifies at about  $5-10^{\circ}\text{C}$ . higher than red oil.

#### END USES OF TECHNICAL OLEIC ACID

In 1948, approximately 68,900,000 lb. of commercial-grade oleic acid (red oil) was produced in the U.S. Of this, about 15,600,000 lb. was used in the preparation of soaps for various textile applications. About 11,900,000 lb. of red oil was used as such for lubrication of textile fibers. It was also used in the manufacture of lubricants and greases (3,200,000 lb.), sulfonated oils (3,800,000 lb.), synthetic detergents (3,200,000 lb.), rubber (1,700,000 lb.), intermediates (2,000,000 lb.), protective coatings (1,700,000 lb.), resins (2,100,000 lb.), metalworking operations (2,400,000 lb.), and miscellaneous industrial applications (2,800,000 lb.). In November 1949, the price of red oil was  $13\frac{1}{2}\text{¢/lb.}$ , and improved technical (low-linoleic) oleic acid was  $14\frac{1}{2}\text{¢/lb.}$ , both in tank cars.

#### DERIVATIVES

Because of its impure nature and especially because of its high linoleic acid content, red oil is not a satisfactory raw material for the preparation of most derivatives of oleic acid and few have been produced, chiefly salts (see Vol. 5, p. 208) and esters (see Vol. 5, p. 830). However, now that a "low-linoleic" type of technical oleic acid is being produced in commercial quantities, many useful derivatives can be made available.

**Oleyl alcohol** (*cis*-9-octadecen-1-ol),  $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_8\text{OH}$ , formula weight 268.47, is the most abundant of the naturally occurring unsaturated alcohols; m.p.  $5.5-7.5^{\circ}\text{C}$ .; b<sub>5</sub>  $187-188^{\circ}\text{C}$ .;  $d_4^{20}$  0.8489;  $n_D^{20}$  1.4606. It is widely distributed in marine-animal oils. It has been reported to constitute 66-70% of the alcohols of sperm-body oil, and these alcohols are at present the principal commercial source. Oleyl alcohol can be prepared from esters of oleic acid by reduction with metallic sodium. For laboratory preparation, the butyl ester dissolved in butyl alcohol is preferred and good yields can be obtained. For industrial application, the sodium can be suspended in a

hydrocarbon solvent like xylene and the alcohol solution of the ester and more xylene added to this suspension as is done in the production of alcohols from the glycerides of coconut oil. Oleyl alcohol can also be prepared from oleates by catalytic hydrogenation with catalysts like copper-cadmium, zinc chromite, ferric chromite, cadmium chromate, zinc vanadium oxide or zinc chromium oxide. Technical oleyl alcohol (Ocenol) is available in 360-lb. steel drums.

Oleyl alcohol can be used in the preparation of esters suitable for use as plasticizers and ingredients of synthetic waxes. With ethylene or propylene oxide, it condenses to give hydroxy ethers with desirable surface-active properties. With concentrated sulfuric acid, it yields the sulfuric acid ester of 1,9-octadecanediol, a surface-active compound. The reaction of acetylene with oleyl alcohol gives vinyl oleyl ether, which is polymerizable and copolymerizable with other vinyl monomers.

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JOHN T. SCANLAN

### Elaidic Acid, $C_{18}H_{34}O_2$ .

Elaidic acid (*trans*-9-octadecenoic acid), formula weight 282.46, is a white solid; it has not been found in nature but is produced when its *cis* isomer, oleic acid, is treated with isomerizing agents, such as oxides of nitrogen, mercurous nitrate, sulfurous acid, sodium hydrogen sulfate, phosphorous acid, and tellurium and selenium and their compounds. Of the catalysts that have been investigated, selenium appears to be by far the most effective. The process may be applied to either oleic acid or its esters using about 0.3% of selenium at 150-220°C. The product is an equilibrium mixture containing about 66% elaidic and 34% oleic acid, and the same equilibrium mixture is obtained when elaidic acid is the starting material. The elaidic acid is readily purified by several crystallizations from acetone at -20°C., followed by a final recrystallization at about -5°C.

Elaidic acid is not a commercial product, but it is interesting that Poutet early in the nineteenth century found that the consistency of olive oil was made comparable to that of hog fat by treatment with mercurous nitrate.

JOHN T. SCANLAN

### Vaccenic Acid, $C_{18}H_{34}O_2$ .

Vaccenic acid (*trans*-11-octadecenoic acid), formula weight 282.46, is a white solid and is the only known naturally occurring *trans* acid. Vaccenic acid has been isolated from beef fat, mutton fat, pork fat, and butter. The percentages recovered have been small, ranging from 0.2 to about 5%. It has also been reported in whale oil and menhaden oil. The fact that vaccenic acid has the *trans* configuration is well established: Its infrared spectrum shows the characteristic absorption band for the *trans* double bond, and a synthesis reported to give the *cis* configuration yields an 11-octa-

decanoic acid melting at 10.5–12°C., which yields, when isomerized with selenium, an acid melting at 43–44°C. Numerous attempts to prepare vaccenic acid by selective hydrogenation of the eleostearic acids have resulted in the production of mixtures of octadecenoic acids containing some of the *trans*-11-isomer. The fact that this impure product gives sharp mixed melting points with the authentic natural product has proved somewhat misleading. This phenomenon of mixtures with sharp melting point is not unusual with long-chain compounds of this type.

A great deal of work has been done on the occurrence and structure of vaccenic acid because it was reported to have growth-promoting properties. It is now known that it does not have such properties. Vaccenic acid is not produced commercially.

JOHN T. SCANLAN

### Erucic Acid and Brassidic Acid, $C_{22}H_{42}O_2$ .

Erucic acid (*cis*-13-docosenoic acid), formula weight 338.56, is a white solid, which was first isolated from mustard-seed oil. Erucic acid is one of the principal constituents of the seed fats of the Cruciferae and the Tropaeolaceae: rapeseed oil contains 43–65%; wallflower-seed oil, 41%; mustard-seed oil, 42%; and jamba oil, 46%. Nasturtium-seed oil has been reported to contain 82%. Erucic acid is converted to the *trans* form (brassidic acid) by treatment with dilute nitric acid, nitrous acid, dilute nitric acid containing sodium nitrite, sulfurous acid, or sulfur. Because of the great commercial importance of rapeseed oil, especially in Europe, erucic acid has received intensive study. It is reputed to be more difficult to isolate than oleic acid and it is not available commercially as the free acid.

JOHN T. SCANLAN

### Sorbic Acid, $C_6H_8O_2$ .

Sorbic acid (2,4-hexadienoic acid), formula weight 112.06, is a white, crystalline solid obtained from unripe sorb apples (mountain ash berries). Sorbic acid is soluble in many organic solvents and, although it is only slightly soluble in water (0.2% by weight), its sodium, potassium, barium, and ammonium salts dissolve readily.

*Reactions.* Sorbic acid takes part in reactions typical of compounds containing conjugated double bonds as well as in the reactions characteristic of carboxylic acids.

Sorbic acid reacts with ammonium hydroxide to form the amide; under pressure this reaction yields diaminocaproic acid amide, the acid of which is isomeric with the amino acid lysine. Primary amines such as *n*-butylamine react with sorbic acid at high temperatures to yield substituted amides first; the amines then add to the conjugated bonds to give amino derivatives of the substituted amides. Monoethanolamine yields *N*-2-hydroxyethylsorbamide, and diethanolamine and acetic anhydride give *N,N*-bis(2-acetoxyethyl)sorbamide,  $CH_3CH:CHCH:CHCON(CH_2CH_2OOCCH_3)_2$ . The product from 2-diethylaminoethanol and sorbic acid is the ester, 2-diethylaminoethyl sorbate. With hydroxylamine, sorbic acid undergoes a peculiar reaction to form acetylacetone dioxime.

Partial hydrogenation of sorbic acid gives hydrosorbic acid (3-hexenoic acid) and, to a lesser extent, the 2,3- and 4,5-addition products.

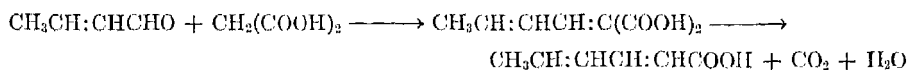
With chlorine, the principal product from sorbic acid is 4,5-dichloro-2-hexenoic acid, and with liquid hydrogen chloride, 5-chloro-3-hexenoic acid is formed at high

temperatures and pressures. Dilute hypochlorous acid yields a mixture of 4-hydroxy-5-chloro-2-hexenoic acid and its lactone (3,5). One molecule of bromine adds to sorbic acid in a carbon disulfide or glacial acetic acid solution to give primarily a crystalline 3,4-dibromohexenoic acid along with a smaller quantity of a 1,2-dibromo derivative (5). With two molecules of bromine, a tetrabromide is formed.

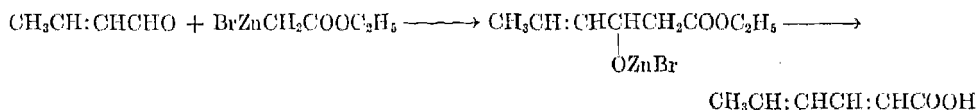
When oxidized by chemical reagents such as potassium permanganate or chromate, sorbic acid undergoes cleavage at the double bonds, a variety of products being reported: carbon dioxide, formaldehyde, acetic acid, oxalic acid, and tartaric acid. Organic peracids, like peracetic and perbenzoic acids, attack the double bond in the 4,5-position, yielding 4,5-epoxy-2-hexenoic acid,  $\text{CH}_3\text{CH}[\text{O}]\text{CHCH}:\text{CHCOOH}$ .

Sorbic acid undergoes the Diels-Alder reaction with many compounds. For example, with maleic anhydride it yields an isomer of 3-methyl-1,2,3,6-tetrahydrophthalic acid (6). It also polymerizes, without catalysts or prolonged heating, presumably by a similar type of mechanism. It copolymerizes with many unsaturated monomers, such as the vinyls and acrylates.

*Manufacture.* Sorbic acid can be made by condensing crotonaldehyde and ketene (4) in the presence of suitable condensation catalysts, such as boron trifluoride (11), followed by destructive distillation at reduced pressure. It has also been synthesized by condensing crotonaldehyde with malonic acid:



Crotonaldehyde and the zinc derivative of ethyl bromoacetate also yield sorbic acid by the Reformatsky reaction:



Other syntheses of sorbic acid include the oxidation of 2,4-hexadienal,  $\text{CH}_3\text{CH}:\text{CHCH}:\text{CHCHO}$ , with silver compounds (1), and the sodium hypochlorite oxidation of 3,5-heptadien-2-one,  $\text{CH}_3\text{CH}:\text{CHCH}:\text{CHCOCH}_3$ .

*Uses.* Glycerides and some other esters of sorbic acid resemble animal fats and vegetable oils. Such esters as allyl sorbate and glycol disorbate (2), which dry rapidly to hard films on exposure to air, are of great interest to the paint and varnish industry as synthetic, quick-drying oils. Esterification is the basis for the most promising applications of sorbic acid, that is, its use in the "upgrading" or improvement of natural drying oils. By means of ester-exchange reactions between linseed oil, glycerol, and sorbic acid (7,9,10), an oil with drying properties equivalent to those of tung oil can be obtained. Soft oils, such as soybean oil, can be improved to attain the properties of dehydrated castor oil by the incorporation of 8% sorbic acid. The properties of tung oil itself can be enhanced by sorbic acid modification. The characteristics of the individual oils may be controlled over a wide range by varying the proportions of sorbic acid and natural oils.

The addition of sorbic acid to coatings of the alkyd type gives smooth flow-out and increased gloss to the finish.

Sorbic acid and its salts and esters have been found to have special merit for inhibiting the growth of microorganisms, particularly molds (8)



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J. A. FIELD

Linoleic Acid,  $C_{18}H_{32}O_2$ .

Linoleic acid (*cis*-9,*cis*-12-octadecadienoic acid), formula weight 280.43, is a colorless, odorless liquid when pure. It occurs widely in land-animal and vegetable oils as the mixed triglyceride with other fatty acids. The important linoleic-rich oils are soybean (55%), cottonseed (50%), corn (40%), linseed (20%), perilla (20%), and tall oil (45%). Linoleic-rich oils are important drying and semidrying oils used in protective coatings (see *Drying oils*; *Fats and fatty oils*). Various edible oils and fats also contain linoleic acid. The mixed fatty acids of oils containing linoleic acid are purified commercially by fractional or simple vacuum distillation. The raw material for the production of these distilled fatty acids is usually a mixture of fatty acids and oil obtained as a by-product from the alkali refining of the crude oils. Linoleic-rich oils are mostly used in protective-coating finishes and in liquid and gel soaps, greases, and metallic drier soaps (see *Driers and metallic soaps*).

**Reactions.** Esterification is the most important reaction of linoleic acid. The simple esters of monohydric alcohols are easily prepared by direct catalytic esterification or by acid- or alkali-catalyzed alcoholysis of linoleic-rich oils. Laboratory fractional distillation for analysis of the fatty acid composition of oils is usually done on the methyl or ethyl ester mixture. The esters made from polyhydric alcohols and polybasic acids are important as drying oils and drying alkyd resins. The acid chloride, amide, nitrile, and salts are formed in the usual manner.

The double bonds show the simple additions to be expected. Hydrogenation first reduces linoleic acid to oleic acid and 12-octadecenoic acid and then to stearic acid. Linoleic-containing glyceride oils are hydrogenated to harden them to plastic fats.

Bromine reacts with linoleic acid to form a mixture of two tetrabromides in approximately equal amounts (14,17). One of these is crystalline, m.p. 115°C., and can be purified by recrystallization. This tetrabromide can be debrominated by zinc to form linoleic acid, and this is the usual laboratory method for preparing pure linoleic acid. However, there is evidence that the linoleic acid prepared in this manner contains some 10–15% of an isomeric form, probably with one of the double bonds changed to the *trans* configuration. Low-temperature solvent crystallization of the debrominated linoleic acid removes this impurity and affords the purest linoleic acid that has been prepared. Almost pure linoleic acid has also been prepared by exhaustive crystallization of linoleic-rich mixtures (8).

Hydroxylation of the double bonds by alkaline permanganate produces two tetra-

hydroxystearic acids ( $\alpha$ - and  $\beta$ -sativic acids) in approximately equal amounts, m.p. 163.5 and 174°C., respectively (15,24).

Maleic anhydride adds to methyl linoleate. When excess anhydride is heated with the ester at 200°C., two moles of anhydride add per mole of linoleate. The first mole saturates a double bond, probably by inducing conjugation, followed by a Diels-Alder reaction. The second mole adds by substitution, since the final adduct contains one double bond (3).

Autoxidation, or oxidation with atmospheric oxygen, is an important reaction of linoleic acid esters. The first steps in the autoxidation are now believed to lead to the formation of a hydroperoxide, with a shift of a double bond to give some conjugated hydroperoxide (see p. 214). The mechanism of autoxidation beyond this peroxide stage is not well known. Free radicals intermediate in peroxide formation, or generated by decomposition of the peroxide may unite to form dimers or polymers. The conjugated double bond systems may unite by a Diels-Alder condensation, by a peroxide-catalyzed vinyl-type polymerization, or by further oxidation to form a polymeric peroxide. The hydroperoxide may also cleave to produce unsaturated aldehydes, which may be responsible in part for rancidity or off-flavors in oxidized edible oils.

Thermal polymerization of linoleic acid or its esters is an important reaction in the heat bodying of linoleate oils (see *Drying oils*). The mechanism apparently involves a shift to a conjugated form, followed by a dimerization by way of a Diels-Alder condensation (5). The dieneophile may be either the double bond of another conjugated linoleate or of an unchanged linoleate. Since conjugation may occur two ways (to 9,11- or 10,12-), and the condensation may occur at the 9,10-, 11,12-, 10,11-, or 12,13-double bond of conjugated or nonconjugated linoleate, a large number of isomeric dimers are possible. The mixture of dimers and trimers of linoleic acid is used commercially to prepare a heat-sealing polyamide resin by reaction with ethylenediamine (1,7).

#### ISOMERS OF LINOLEIC ACID

Ordinary linoleic acid, which is *cis*-9,*cis*-12, may be changed to the *trans*-9,*trans*-12-form by the action of selenium at 200°C. or by the action of oxides of nitrogen. The **linolelaidic acid** thus produced (in small yields) is a crystalline material. The *cis*-9,*trans*-12- and *trans*-9,*cis*-12-forms are also probably formed to some extent, but have not been isolated in sufficiently pure form to be characterized (11).

The action of alkali at elevated temperatures causes ordinary linoleic acid to change to conjugated forms. These are apparently mixtures of 9,11- and 10,12-octadecadienoic acids. Presumably, the double bond which shifts may become *cis* or *trans* in its new position, so these forms are probably *cis*-9,*cis*-and-*trans*-11 and *cis*-and-*trans*-10,*cis*-12 (9,10). Alkali-produced conjugated acids have been made commercially.

Dehydrated-castor-oil acids consist of a mixture of 9,11- and 9,12-octadecadienoic acids, resulting from the loss from ricinoleic acid of water between the hydroxyl group on C<sub>12</sub> with a hydrogen on C<sub>11</sub> or C<sub>13</sub>, respectively. The 9,12-acid is apparently not entirely identical with normal linoleic (23), and is probably a mixture of *cis*-9,*trans*-12 with *cis*-9,*cis*-11 and *cis*-9,*trans*-11, since the double bond in ricinoleic acid is *cis* (9). Dehydrated castor oil and dehydrated-castor-oil acids are produced commercially for use in protective coatings (see *Castor oil*).

By dehydration of elaidinized ricinoleic acid, a crystalline 9,11-octadecadienoic acid, m.p. 54°C., has been isolated, presumably a *trans-trans* form (22).

A 10,12-octadecadienoic acid, m.p. 57°C., which is apparently trans-trans, has been isolated from the alkali-isomerized acids of dehydrated castor oil (23). The formation of a 10,12-octadecadienoic acid, m.p. 29°C., has been reported by the 1,6-addition of one mole of hydrogen to eleostearic acid (9,11,13-octadecatrienoic acid) (4).

A liquid 8,10-acid has been reported to result from the dehydrohalogenation of 9,10-dibromo- or dichlorostearic acid with 20% potassium hydroxide at 100°C. (16).

Partial hydrogenation of ordinary linolenic acid (*cis*-9,*cis*-12,*cis*-15-octadecatrienoic acid) results in the formation of an isomer of linoleic acid, the exact nature of which has not been determined. It might be the 9,15-isomer, and *cis*-trans isomerization may also be involved (13).

The synthesis of linoleic acid has been reported. The final product was a mixture that failed to yield the crystalline tetrabromide characteristic of normal linoleic acid. The presence of some normal linoleic acid was indicated by hydroxylation and isolation of the tetrahydroxystearic acids (in low yields) characteristic of normal linoleic acid (20).

#### ANALYSIS

In simple binary mixtures with other known acids, linoleic may be determined by a measure of the iodine value. Since simple binary mixtures seldom occur, other values in conjunction with iodine value are needed. For example, by determining the iodine value and thiocyanogen value of mixtures of linoleic, oleic, and saturated acids, the composition may be calculated. When linolenic acid is present, it is also necessary to determine the percentage of saturated acids independently in order to calculate the composition (12, 18, 21).

The quantitative isolation of the crystalline tetrabromostearic acid produced by bromination under controlled conditions has been used as a method of determination of linoleic acid (17). With mixtures low in linoleic acid the method is limited by the solubilizing effect of the liquid bromides concurrently formed.

Ultraviolet absorption is a relatively new and very valuable method for determining linoleic acid in mixtures. Ordinary linoleic acid, being nonconjugated, does not absorb appreciably in the near-ultraviolet region. By heating in alkaline solutions at elevated temperatures under definite conditions, linoleic acid is converted extensively and reproducibly to a mixture of conjugated forms, which absorb strongly at about 2300 Å., characteristic of diene conjugation (see Table XV, p. 198). Oleic acid and saturated acids do not interfere. Linolenic acid also develops some diene conjugation for which correction can be made, since there is a constant ratio between the amount of diene and triene conjugation formed from linolenic acid. This triene conjugation is measured by the absorption of about 2700 Å. (where diene does not absorb appreciably) and correction of the absorption at 2300 Å. can be made. From this corrected absorption at 2300 Å. the percentage of linoleic acid can be calculated from known constants determined on pure linoleic acid (2,6,10,19).

Ultraviolet absorption is also valuable in estimating the amount of conjugation existing in unsaturated acids before the analytical isomerization. Absorption at 2300 Å. without isomerization is indicative of diene conjugation (6,10). By this method, dehydrated castor oil is shown to contain 20-30% of conjugated linoleate (10), and the development of diene conjugation during thermal polymerization and autoxidation has been followed. (See also "Spectral properties," p. 195.)

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D. H. WHEELER

Linolenic Acid,  $C_{18}H_{30}O_2$ .

Linolenic acid (*cis*-9,*cis*-12,*cis*-15-octadecatrienoic acid), formula weight 278.42, is a colorless, odorless liquid when pure. It occurs as the mixed triglyceride with other fatty acids in vegetable oils, particularly the drying oils. The important linolenic oils are linseed (50%) and perilla (55%). Soybean oil contains about 5%. Linseed oil is the most important drying oil used in protective coatings and its rapid drying is largely attributable to the highly unsaturated linolenate present (see *Drying oils*; *Fats and fatty oils*). Linolenic-rich fatty acids are produced by vacuum distillation of the crude acids obtained from refining by-products or from hydrolysis of the oil itself. Linolenic-rich acids are not produced in such a large volume as the linoleic-rich acids, because the linolenic-rich oils are not subjected to refining on the scale followed with linoleic-rich oils. Linolenic-rich acids are used in protective coatings, in liquid and gel soaps, and in metallic drier soaps (see *Driers and metallic soaps*).

**Reactions.** Hydrogenation of linolenic acid produces stearic acid, with linoleic and oleic acids and their isomers as intermediates (11).

Addition to the double bonds with bromine yields a crystalline hexabromide, m.p. 180°C., in a maximum yield of 35%. Debromination with zinc forms linolenic acid. This is the usual laboratory method of preparing pure linolenic acid (12,15). Linolenic acid prepared in this manner apparently contains 15-20% of an isomer, presumably with one or more of the double bonds elaidinized. Repeated low-temperature solvent crystallization of the debrominated linolenic acid removes this isomer and affords pure

linolenic acid, which is apparently identical with the purest linolenic acid obtained by exhaustive crystallization of linolenic-rich acid mixtures (13).

Hydroxylation of the double bonds with alkaline permanganate affords low yields of two crystalline hexahydroxy acids ( $\alpha$ - and  $\beta$ -linusic acids), m.p. 173° and 203°C., respectively.

Almost three moles of maleic anhydride add to methyl linolenate when excess maleic anhydride is used at 200°C. The first two moles add to saturate two double bonds, probably by inducing conjugation, followed by a Diels-Alder reaction. The third mole adds by substitution without saturating the remaining double bond (2). Maleic-treated drying oils, further condensed with a polyhydric alcohol, have improved drying properties and have been produced commercially (see also *Maleic acid and maleic anhydride*).

The autoxidation of linolenic esters follows a mechanism similar to that described for linoleic esters (see p. 275). Autoxidation is much more rapid than with linoleates, which accounts for the more rapid drying of linolenic oils (6). In addition to diene-conjugated hydroperoxides as in case of linoleates, there is evidence that some triene conjugation is formed, presumably by a corresponding shift of the third double bond into a conjugated position with respect to the conjugated diene first formed. The same general speculations apply to the further course of oxidative polymerization beyond the peroxide stage as was described for linoleates.

Thermal polymerization of linolenic esters is an important reaction in the production of varnishes and heat-bodied linseed oils. The mechanism is similar to that followed by linoleates, namely, a shift to a conjugated form, followed by dimerization by way of a Diels-Alder condensation (3). Since a linolenate can form a larger number of isomeric conjugated forms, the number of possible isomeric dimers is even greater than with linoleates. Moreover, there is some evidence that intramolecular ring closure follows the initial dimerization of linolenates resulting in a bicyclic or tricyclic dimer (3). Because linolenates polymerize much more rapidly than linoleates, and there is formed a higher percentage of trimer, linolenic oils body much faster than linoleic oils.

#### ISOMERS OF LINOLENIC ACID

By the action of selenium at 200°C., normal linolenic acid is converted to the elaidinized form, **elaidolinolenic acid** (*trans*-9,*trans*-12,*trans*-15-octadecatrienoic acid) (9).

Alkali at elevated temperatures partially converts normal linolenic acid to a conjugated isomer, apparently **pseudoeleostearic acid** (*trans*-10,*trans*-12,*trans*-14-octadecatrienoic acid). There is also formed a considerably greater amount of triene acids with diene conjugation, presumably the 9,11,15- and 9,13,15-isomers of linolenic acid (8). See also "Eleostearic acid" (p. 279), the naturally occurring isomer of linolenic acid.

#### ANALYSIS

The use of the thiocyanogen absorption in conjunction with the iodine value for analyzing mixtures of oleic, linoleic, and linolenic acids has been discussed under linoleic acid (see p. 276).

The quantitative isolation of the crystalline hexabromide produced by bromination under controlled conditions has been used for estimating linolenic acid (13).

The most useful method now available is ultraviolet-absorption measurement after alkali isomerization under controlled conditions. The absorption with a peak at about 2700 Å., characteristic of triene conjugation (see Table XV, p. 198), is a direct measure of linolenic acid. Oleic, linoleic, or saturated acids do not interfere. More highly unsaturated acids interfere and correction must be made for their effects, if present (1,4,7). Ultraviolet absorption in the 2700 Å. region (without isomerization) may be used to estimate conjugated isomers of linolenic acid in mixtures with non-conjugated acids (4,7,14).

The determination of the addition of maleic anhydride has also been used to estimate the amount of conjugated acids in the presence of nonconjugated acids (5,10). This method is not as specific as spectral analysis, since it does not differentiate between diene and triene conjugation, and certain cis-trans isomers do not react quantitatively.

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D. H. WHEELER

### Eleostearic Acid, $C_{18}H_{30}O_2$ .

Eleostearic acid (elaostearic acid, 9,11,13-octadecatrienoic acid), formula weight 278.42, is a white crystalline solid, soluble in alcohol and in most organic solvents. It is the most important isomer of linolenic acid, and all three double bonds are in conjugated positions. Three geometric isomers of 9,11,13-octadecatrienoic acid are known:  $\alpha$ -eleostearic acid, m.p. 48-49°C., which is the chief acid of tung oil;  $\beta$ -eleostearic acid, m.p. 71°C.; and punicic acid, m.p. 43.5-44°C., from pomegranate-seed oil.  $\beta$ -Eleostearic acid is formed from either of the other two acids by the action of ultraviolet light or catalysts such as iodine or sulfur, but has never been converted to the other two forms. The configurations of these isomers have not been definitely proved. The  $\alpha$ -isomer has been generally assumed to be the cis-9-cis-11-trans-13, and the  $\beta$ -isomer to be the trans-9-cis-11-cis-13. For positional isomers of eleostearic acid, see "Linolenic acid," p. 278.

$\alpha$ -Eleostearic acid comprises 80-85% of the fatty acids in tung or China wood oil, an important drying oil (*g.v.*). It is also a major constituent of the oils obtained from *Garcia nutans*, essang, po-yoak, neou, behuroda, krobanko, taritch, *Aleurites cordata*, and *A. trisperma*, and it is present in oiticica oil and some other oils.

*Physical and Chemical Properties.* The eleostearic acids are characterized by exalted molecular refractivities resulting from the conjugated positions of their double bonds.  $\alpha$ -Eleostearic acid: viscosity at 50°C., 33.42 poises; molar refractivity, 92.36; parachor value, 741.  $\beta$ -Eleostearic acid: viscosity at 75°C., 31.04 poises; molar refractivity, 92.2; parachor value, 736.9.

Owing to the conjugated double bonds, eleostearic acid and its glycerides polymerize readily when heated, forming elastic gels. The acid is also extremely unstable on exposure to light, air, etc., and must be protected from oxidation-polymerization by air.  $\alpha$ -Eleostearic acid absorbs oxygen at a rate of 2.68 and the  $\beta$ -isomer at a rate of 1.02, compared with linolenic acid, the nonconjugated isomer, which absorbs oxygen at a rate of 0.52, expressed in moles of oxygen per mole of acid per 100 minutes. Eleostearic acid apparently does not form a hydroperoxide, as do linoleic and linolenic acids, but may form polymeric peroxides directly.  $\alpha$ -Eleostearic acid on oxidation at room temperature with dilute potassium permanganate ( $\pm 8\%$ ) containing a small amount of sodium carbonate yields azelaic, valeric, and oxalic acids, while ozonation yields valeraldehyde, valeric acid, and azelaic acid. The geometrically isomeric punicic acid, upon oxidation at 0°C. with a 10% aqueous acetone solution containing 3% potassium permanganate and 2% sodium carbonate, yields azelaic and valeric acids and some oxalic acid, whereas ozonation yields azelaic, valeric, and oxalic acids, and glyoxal.

Hydrogenation of eleostearic acid with one mole of hydrogen yields an acid containing a conjugated system of two double bonds as indicated by the disappearance of the triene conjugation and the appearance of diene conjugation with a decrease in the maximum absorption at 270 m $\mu$  and an increase in absorption at 230 m $\mu$  (see Table XV, p. 198). Complete hydrogenation of eleostearic acid yields stearic acid.

Both  $\alpha$ - and  $\beta$ -eleostearic acids react with one mole of maleic anhydride to form crystalline Diels-Alder adducts melting at 62.5 and 77°C., respectively. These adducts, upon oxidation with potassium permanganate and acetone, yield azelaic and valeric acids, respectively, as chief products, indicating that addition of maleic anhydride occurred in the  $\alpha$ -acid at C<sub>11</sub> and C<sub>14</sub>, while in the  $\beta$ -acid addition occurred at C<sub>6</sub> and C<sub>12</sub> (3).

Eleostearic acid adds two moles of halogen and a third mole only slowly and with difficulty. The tetrabromide melts at 113.5–114°C., and is formed also by punicic acid. A hexabromide prepared by the bromination of eleostearic acid in the presence of ultraviolet light has been reported by different investigators to melt at 139–141 and 157°C. Debromination of the hexabromide with zinc and ethyl alcohol yields  $\beta$ -eleostearic acid.

*Preparation.*  $\alpha$ -Eleostearic acid was prepared by Nicolet by repeated recrystallization of tung-oil fatty acids in half their weight of ethyl alcohol (4). Strain prepared the  $\beta$ -isomer by dissolving tung-oil fatty acids in 85% methanol, isomerizing by the addition of iodine dissolved in absolute methanol, followed by separation of the acid and recrystallization first from 85% methanol and then from absolute methanol (7).

*Analysis.* Two of the double bonds of eleostearic acid add bromine quantitatively in 30 minutes in glacial acetic acid in the presence of pyridine and sulfuric acid (2,6). Thiocyanogen reacts with only one double bond of  $\beta$ -eleostearic acid (2). The eleostearic acid content of an oil can be estimated by the Ellis-Jones maleic anhydride method (1). The proportions of  $\alpha$ - and  $\beta$ -eleostearic acids present in a mixture of the two acids can be determined spectrophotometrically by using the extinction coefficients

at the absorption maxima of the  $\alpha$ - and  $\beta$ -isomers, which occur at 2715 and 2695 Å., respectively (5).

*Derivatives.* Ethyl eleostearate readily polymerizes when it is heated to 280°C. Pentaerythritol eleostearate can be prepared by heating equimolar proportions of pentaerythritol and freshly prepared eleostearic acid in the presence of small amounts of litharge as catalyst for 3.5 hours in a current of carbon dioxide. Mannitol eleostearate can be prepared in a similar manner by heating at 180°C. for 8.5 hours. Lead eleostearate is slightly soluble in ethyl alcohol and ethyl ether.

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R. S. MCKINNEY

### Arachidonic Acid, $C_{20}H_{32}O_2$ .

Arachidonic acid (5,8,11,14-eicosatetraenoic acid), formula weight 304.46, was discovered by Hartley in liver lipides in 1909 (10), and was later named arachidonic acid by J. Lewkowitsch from its resemblance in carbon chain length to arachidic acid and in unsaturation to clupanodonic acid, which was believed at that time to be an octadecatetraenoic acid. Most of the investigative work on arachidonic acid has been done on its methyl ester, because of the somewhat greater stability of the ester. Constants of methyl arachidonate have been found on samples that admittedly contained several per cent of impurity: m.p.,  $< -78^\circ\text{C}$ .;  $b_m$ , 160-165°C.;  $n_D^{20}$ , 1.4825;  $d_4^{20}$ , 0.9082; theoretical iodine value, 319.0.

*Reactions.* Arachidonic acid, an extremely weak acid, forms typical soaps with the alkali and alkaline earth metals. Its lead soap is soluble in ether and in alcohol. The lithium soap is soluble in 95% acetone, which differentiates the acid from oleic, linoleic, and the saturated acids. Partial hydrogenation produces a mixture of 8,14-eicosadienoic and 5,14-eicosadienoic acids (12). Complete hydrogenation yields arachidic acid (13). Because of its polyethenoic nature, arachidonic acid oxidizes rapidly in air. Upon oxidation in cold alkaline solution in water with dilute potassium permanganate, arachidonic acid yields the water-soluble octahydroxyarachidic acid. Ozonolysis yields a tetraozonide, which upon cautious decomposition with aqueous hydrogen peroxide gives the mixture of mono- and dicarboxylic acids which would be predicted from its structure (8,12). Addition of bromine to a cold ethereal solution of the acid or of its methyl ester results in the precipitation of about  $\frac{1}{3}$  of the predicted amount of octabromides; the remaining octabromides, and other material the nature of which has not been determined, remain in solution in ether. The octabromo methyl ester, which melts at 227-230°C., provides a ready means of identification (1). The actual yield of octabromides from one gram of methyl arachidonate has been found to be 0.922 gram (or a polybromide number of 92.2) (17); the theoretical yield is 3.01 grams. Upon treatment with alkali in hot glycerol or ethylene glycol, double-bond rearrangement takes place with formation of tetraene conjugation; the acid thus be-



comes spectroscopically visible in the ultraviolet region, which serves as a basis for its quantitative estimation. Absorption coefficients are as follows: 59.3 at 2340 Å.; 53.4 at 2680 Å.; 25.8 at 3010 Å.; and 22.6 at 3160 Å. (2).

*Occurrence.* The best source of arachidonic acid is the phosphatides of beef adrenal glands, the fatty acids of which contain 20–25% arachidonic acid (1,4). It also occurs in other glandular lipides, such as those in the liver (3), thyroid (3), and corpus luteum (6), and is present in small amounts in the brain (11,15), fish oils, butterfat, human milk fat (4), human body fat (7,9), lard, and, in fact, in most animal fats (5). In some instances it occurs along with other polyethenoid acids as, for example, in the fish oils and in liver lipides.

*Preparation.* Arachidonic acid is not commercially available at present. It is best prepared in the laboratory in the form of its methyl ester, by starting with the mixed methyl esters of the fatty acids of adrenal phosphatides, which are conveniently made by direct alcoholysis. Three methods of isolation may be used: (1) *Bromination-debromination.* The esters are brominated in cold ether solution, and the precipitated methyl ester octabromides are purified by washing with ether; they are then refluxed in methanol with an excess of zinc dust for several hours. The resulting methyl arachidonate is then recovered and distilled *in vacuo*. It should be almost water-white and have a nearly theoretical iodine value (Wijs 1–3 hour reaction). (2) *Crystallization-distillation* (13). An acetone solution (100 grams/liter) of the adrenal esters is cooled to  $-65^{\circ}\text{C}$ . and filtered. The esters in the filtrate are composed of 60–70% methyl arachidonate. Careful fractional distillation yields 90–95% methyl arachidonate (12). (3) *Chromatography* (16). The concentrated esters can be employed to separate the arachidonate from unwanted material by elution chromatography on alumina, carbon, or silica.

*Uses.* To date there are no commercial uses for arachidonic acid and its esters. However, this acid belongs to the nutritionally important group of essential fatty acids, which includes also linoleic and linolenic acids. The three acids are to some extent interchangeable as essential nutrients, but there is some evidence that arachidonic acid is actually formed in the animal liver from the other two acids.

*Derivatives.* 5,6,8,9,11,12,14,15-Octahydroxyarachidic acid,  $\text{C}_{20}\text{H}_{32}\text{O}_2(\text{OH})_8$ , is a white solid, soluble in hot water, from which it crystallizes on cooling; m.p.  $195^{\circ}\text{C}$ .

5,6,8,9,11,12,14,15-Octabromoarachidic acid,  $\text{C}_{20}\text{H}_{32}\text{Br}_8\text{O}_2$ , is a white solid, insoluble in cold ethyl ether, sparingly soluble in hot benzene and in butyl alcohol; the acid contains 67.74% bromine, and darkens without melting at  $230\text{--}250^{\circ}\text{C}$ . Methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-amyl ester octabromides melt at  $227\text{--}230$ ,  $226\text{--}227$ ,  $223\text{--}224$ ,  $222\text{--}223$ , and  $221.5\text{--}222.5^{\circ}\text{C}$ ., respectively (14).

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### MARINE-OIL ACIDS

With the exception of isovaleric acid, all fatty acids found in fish and other marine oils are normal straight-chain compounds. They differ from the fatty acids found in terrestrial-animal and vegetable fats chiefly in the number and complexity of their unsaturated members, which range from the  $C_{10}$  through the  $C_{28}$  series. The unsaturation is largely ethylenic but the possibility that small amounts of acetylenic unsaturation occur cannot be entirely dismissed. The ethylenic bonds are largely nonconjugated, although again there are some data that suggest the possible presence of traces of conjugation. Exaltation of molecular refraction has been consistently observed but the extent of conjugation does not exceed about 2% of the total unsaturation. Finally, the occurrence of a hydroxyoleic acid, an isomer of ricinoleic acid, has been reported. Its distribution, however, appears to be limited to one or two species.

While reasonably precise separations of one carbon series of saturated fatty acids from adjacent even-numbered series are possible by modern methods of fractional distillation, unfortunately the same is not true of a mixture of unsaturated fatty acids of the same carbon series. Usually the best that can be accomplished is the determination of the amount of unsaturated fatty acids in a particular fraction together with their average unsaturation (usually reported in terms of the amount of hydrogen required to saturate the acids completely,  $-2H$  representing one double bond). Separation of the individual unsaturated fatty acids of any one carbon series is then usually accomplished by special techniques, which may include the low-temperature fractional crystallization of salts of the acids in various solvents, separation of bromine addition products, and recently the use of chromatography and the molecular still.

The inherent instability of the more highly unsaturated fatty acids, which may contain up to seven double bonds, complicates isolation and purification before the determination of structure. Up to the present, most of the "pure" acids on which structural work has been done have been obtained by the vacuum distillation of their methyl esters, during which process such esters may have been subjected to temperatures up to  $200^{\circ}C$ . for varying lengths of time. Such treatment has no apparent effect on mono-, di-, and triethylenic acids but both isomerization and polymerization may take place in higher-polyethylenic acids or esters. The application of molecular-distillation techniques to the fatty acid esters of cod-liver oil has resulted in the isolation of a  $C_{22}$  acid with six double bonds. The same oil, when fractionated by ordinary vacuum-distillation processes yielded a  $C_{22}$  fraction with mainly five double bonds.

It is therefore contended by some authorities that polyethylenic acids isolated by vacuum distillation of their methyl esters have at least one double bond less than the acids in the natural state, this double bond being lost by cyclization during distillation. Opponents to this theory point out that such acids always show a straight-chain structure when hydrogenated and thus cannot be presumed to be cyclized. Furthermore, while polymerization practically always occurs during distillation of highly unsaturated esters, the more highly unsaturated polymerize more readily and the

gradual decrease in unsaturation during repeated distillation is due to the removal of these more highly unsaturated members as a polymerization residue. The general view at present is, therefore, that such highly unsaturated acids as have been isolated actually did exist as such in the natural oil but that the presence of even more highly unsaturated members must be admitted as a possibility, (a) if the total unsaturation of the original undistilled fraction is appreciably higher than that calculated from the distilled fractions, and (b) if there is an appreciable polymerized undistilled residue. Such a view confirms the reliability of the large amount of data already available on the occurrence and structure of highly unsaturated fatty acids and explains, in part, the scattered reports throughout the literature of the presence of extremely highly unsaturated acids. It will usually be found, in such cases, that the investigators used a highly efficient fractionating column and succeeded in reducing or practically eliminating the residual polymer.

The determination of the structure of the individual unsaturated fatty acids is, of course, chiefly a matter of locating the positions of the double bonds, since it has been demonstrated fairly conclusively that they are all normal straight-chain compounds. Homogeneity of the carbon series may first be checked by completely hydrogenating a sample and comparing the melting point of the saturated product with an authentic sample of the particular saturated acid of the carbon series being investigated. Position of the double bonds is usually determined by oxidation followed by identification of the scission products. The two general oxidation procedures are ozonolysis and the use of a permanganate-acetone solution. Both procedures are tedious and can yield trustworthy results only in the hands of experienced investigators. In spite of their shortcomings, however, most of our information on the structure of highly unsaturated acids has been obtained by these classical methods.

While in vegetable oils polyethylenic acids are largely restricted to the  $C_{18}$  series, those in fish oils range from  $C_{16}$  to  $C_{26}$ , with the  $C_{20}$  and  $C_{22}$  series predominating. In nearly all of the polyethylenic acids of the  $C_{18}$  series in vegetable oils the first double bond occurs between the 9th and 10th carbon atoms as it does in the predominant monoethylenic acids oleic and palmitoleic. In fish oils, however, although many acids have their first double bond in the 9,10-position, there are many that have it situated closer to the carboxyl group, chiefly in the 4,5-position. Furthermore, while in vegetable-oil fatty acids the ethylenic bonds are usually separated by one methylene group or are conjugated (see Vol. 5, p. 279), fish-oil fatty acids may have their ethylenic bonds separated by two such methylene groups. Such differences in structure are now being recognized as the reason for the peculiar dissimilarities between the chemical properties of fish oils and vegetable oils (see *Fats and fatty oils*).

#### SATURATED ACIDS

Since all of the saturated acids found in fish oils are described in other sections of this article, only their general distribution in fish oils will be mentioned in this section. **Isovaleric acid**,  $C_5H_{10}O_2$ , is the only branched-chain acid and the only acid with an odd number of carbon atoms known to occur in fish oils or marine-animal oils. It is a major component of the acids in the depot fats of the Delphinidae, where it occurs in mixed glycerides with normal straight-chain fatty acids. **Caprylic acid**,  $C_8H_{16}O_2$ , occurs in small amounts in fin-whale blubber oil and in some Japanese herring oils. **Capric acid**,  $C_{10}H_{20}O_2$ , is a minor constituent (about 3%) of the head oil of the sperm whale. **Lauric acid**,  $C_{12}H_{24}O_2$ , is a major constituent (about 16%) of the fatty acids of the head oil of the sperm whale, and a minor constituent of depot fats of Delphinidae. **Myristic acid**,  $C_{14}H_{28}O_2$ , occurs widely in fish oils. Head oil of the sperm whale contains about 15% and depot fats of Delphinidae about 30%. In all other fish oils it

occurs as a minor constituent. **Palmitic acid**,  $C_{16}H_{32}O_2$ , is the most important saturated fatty acid in fish oils and is generally present in an amount of 15%. In some shark-liver oils it is present in amounts up to 40%. **Stearic acid**,  $C_{18}H_{36}O_2$ , is widely distributed in practically all fish oils but in lesser amounts than palmitic acid. **Arachidic acid**,  $C_{20}H_{40}O_2$ , has limited distribution, being found chiefly in liver oils of certain sharks. **Behenic acid**,  $C_{22}H_{44}O_2$ , has a very limited distribution, being found chiefly in some shark-liver oils. **Lignoceric acid**,  $C_{24}H_{48}O_2$ , has limited distribution, with traces found in some sardine and herring oils and in a few shark-liver oils.

#### UNSATURATED ACIDS

**Caproleic acid**,  $C_{10}H_{18}O_2$ , has one double bond in the 9,10-position and thus possesses a terminal methylene group. The acid is found in traces in the head oil of the sperm whale. **Lauroleic acid**,  $C_{12}H_{22}O_2$ , has one double bond variously reported to be in the 3,4- or 5,6-position. It is a minor component of the head oil of the sperm whale and of the depot fats of Delphinidae. **Myristoleic acid and physeteric acid**,  $C_{14}H_{26}O_2$ , are isomeric forms of *n*-tetradecenoic acid. Myristoleic acid with the double bond in the 9,10-position has a wide distribution as a trace component. The 5,6-isomer, physeteric acid, occurs to the extent of about 14% in the head oil of the sperm whale, and to a lesser extent in the blubber oil.

**Palmitoleic acid** (physetoleic acid),  $C_{16}H_{30}O_2$ , has one double bond in the 9,10-position. It is a major component in most fish and other marine-animal oils, and is found in amounts ranging from 10 to 20%. **Hiragonic acid**,  $C_{16}H_{30}O_2$ , has three double bonds reported to be in the 6,7; 10,11; 14,15-positions. It is found in some herring oils.

**Oleic acid and vaccenic acid**,  $C_{18}H_{34}O_2$ , are isomeric forms of octadecenoic acid. Oleic acid, the 9,10-variety, has very wide distribution, and is usually present as a major constituent. Vaccenic acid, the 11,12-isomer, has been reported to be present in whale oil and menhaden oil. A hydroxyoleic acid, apparently isomeric with ricinoleic acid, has been reported to be a major component of the "castor-oil fish," *Ruvettus pretiosus*. **Octadecadienoic acid**,  $C_{18}H_{32}O_2$ , if present at all in fish oils, is not ordinary linoleic acid common in vegetable oils, which is the 9,10;12,13-isomer. **Octadecatrienoic acid**,  $C_{18}H_{30}O_2$ , has been reported to be present in fish oils. The acid or acids are probably isomers of ordinary linolenic acid. **Morotctic acid**,  $C_{18}H_{28}O_2$ , has double bonds in the 4,5;8,9;12,13;15,16-positions. It has been reported to be present in the head oil of the white whale and in small amounts in Japanese sardine oil.

**Gadoleic acid**,  $C_{20}H_{38}O_2$ , has one double bond in the 9,10-position. The acid is widely distributed in most species but the proportion is not accurately known. An isomer of unknown structure has been reported in the oil of the pilot whale. **Eicosadienoic acid**,  $C_{20}H_{36}O_2$ , has double bonds in the 11,12;14,15-positions. It is a minor constituent in oils of several species of fish.

**Eicosatrienoic acid**,  $C_{20}H_{34}O_2$ , has double bonds in the 8,9;11,12;14,15-positions. It is a minor constituent in various fish oils. **Eicosatetraenoic acid**,  $C_{20}H_{32}O_2$ , is of general occurrence in fish oils. Two isomers with the double bonds in the 4,5;8,9;12,13;16,17-positions and 6,7;10,11;14,15;18,19-positions have been isolated and identified. Neither of these is identical with the arachidonic acid of vegetable oils, which is the 5,6;8,9;11,12;14,15-isomer. **Eicosapentaenoic acid**,  $C_{20}H_{30}O_2$ , has double bonds in the 4,5;8,9;12,13;14,15;18,19-positions. It is a major component of most fish oils.

**Cetoleic acid**,  $C_{22}H_{42}O_2$ , has one double bond in the 11,12-position. It is most

abundant in certain shark-liver oils and is widely distributed in other fish oils as a minor component, but is absent from the depot fats of fresh-water fish and, in general, from the depot fats of sharks, where the  $C_{22}$  unsaturated acids are entirely polyethylenic. **Docosadienoic acid**,  $C_{22}H_{40}O_2$ , with double bonds in the 11,12;14,15-positions, has recently been reported to be present in shark-liver oil. **Docosatrienoic acid**,  $C_{22}H_{38}O_2$ , with double bonds in the 8,9;11,12;14,15-positions has recently been found in shark-liver oils. **Clupanodonic acid**,  $C_{22}H_{34}O_2$ , has been the subject of much controversy. The acid actually isolated has double bonds probably in the 4,5;8,9;12,13;15,16;19,20-positions. It is widely distributed in fish oils and marine-animal oils, sometimes as a major component. **Docosaheptaenoic acid**,  $C_{22}H_{32}O_2$ , is closely associated with clupanodonic acid. Some authorities claim it is the parent substance from which clupanodonic acid is finally obtained during isolation, but its structure is not established. It is apparently of wide distribution in all marine-animal oils.

**Selacholeic acid** (nervonic acid),  $C_{24}H_{46}O_2$ , has one double bond in the 15,16-position. It is the characteristic component of many oils of elasmobranchs. Minor and trace components are found in some oils from teleosts. **Scoliodonic acid** (tetracosapentaenoic acid),  $C_{24}H_{38}O_2$ , is of unknown structure. It is a minor component in shark-liver oils. **Nisinic acid**,  $C_{24}H_{36}O_2$ , with double bonds reported to be in 4,5;8,9;12,13;15,16;18,19;21,22-positions, is a minor constituent of Japanese sardine oil. **Bonotonic acid** (tetracosaeptaenoic acid),  $C_{24}H_{34}O_2$ , is reported to be present in the body oils of the bonito.

**Shibic acid** (hexacosapentaenoic acid),  $C_{26}H_{42}O_2$ , is reported to be present in small amounts in liver oils of the bluefin tuna and related fish. **Thynninc acid** (hexacosahexaenoic acid),  $C_{26}H_{40}O_2$ , is of unknown structure. Its presence in the liver oils of the bluefin tuna and related species was recently claimed.

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## HYDROXY AND KETO ACIDS

### HYDROXY-SUBSTITUTED ACIDS

Hydroxy-substituted fatty acids accompany all normal fats, but, with the exception of ricinoleic acid (see p. 290), the hydroxy acids do not occur in sufficient amounts to be of economic importance. They form in liquid fats by air oxidation in the light and can be isolated in crystalline form from the precipitate that often appears in oils after long standing. Table I gives the occurrence of the more important hydroxy-substituted fatty acids.

Polyhydroxy fatty acids are soluble in hot water and in alcohol, less soluble in ether, and insoluble in petroleum ether. Branching of the paraffin chain or the presence of other normal fatty acids makes them more soluble. Hydroxy fatty acids are relatively stable, although 4- and 5-hydroxy acids are stable only in the cold. On slightly

warming, they form internal lactones, having melting points about 40°C. lower than those of the corresponding acids.

All hydroxy fatty acids on warming with water-splitting substances like sulfuric acid yield unsaturated fatty acids. By splitting two molecules of water from vicinal dihydroxy fatty acids, conjugated double-bond fatty acids can be produced, usable as drying oils. Hydroxy acids undergo the reactions characteristic of carboxylic acids and alcohols. Of particular importance is the tendency for inter- and intramolecular esterifications. The ease with which these occur is determined by the position of the hydroxyl group in the carbon chain.

Monohydroxy fatty acids may be prepared by the following methods: (1) by the action of aqueous alkali hydroxides on halogen-substituted fatty acids (sometimes complicated by dehydrohalogenation to yield an unsaturated acid, or by lactone formation); (2) by addition of sulfuric acid to the double bonds of unsaturated fatty acids followed by hydrolysis of the sulfated fatty acid (as two isomers form, purification is difficult); and (3) by reduction of well-defined keto acids. All of the monohydroxystearic acids have been synthesized by Bergström (1).

Vicinal dihydroxy fatty acids and tetra- and hexahydroxy fatty acids are formed by oxidation at the double bonds of unsaturated fatty acids with potassium permanganate, hydrogen peroxide, or osmium tetroxide under mild conditions. Cis unsaturated fatty acids yield a mixture of the higher-melting *DL-erythro* (or *cis*)-dihydroxy fatty acids (all melting from 115 to 135°C.), while the trans acids give the *DL-threo* (or *trans*)-dihydroxy fatty acids (melting from 70 to 100°C.).

#### KETO-SUBSTITUTED ACIDS

Keto-substituted fatty acids are rarely found in nature, and, with the exception of licanic acid (see p. 295), are of little industrial importance. Knowledge of the keto acids is largely confined to synthetic products. 3-Keto fatty acids are intermediate products in fatty acid catabolism. The resulting methyl ketones, especially the lower fatty acids, contribute to the rancidity of fats. The methyl ketones of C<sub>6</sub>-C<sub>12</sub> acids are components of some plant oils, such as *Oleum rutae*. Higher keto fatty acids, formed as condensation products of normal fatty acids, are assumed to be the biochemical predecessors of plant waxes (5).

The melting points of keto fatty acids are about 10–20°C. higher than those of the corresponding unsubstituted fatty acids. The solubilities of keto fatty acids in organic solvents are nearly the same as with normal fatty acids.

Keto acids show the reactions of both the keto group and the carboxyl group. Their properties depend to a considerable extent upon the position of the keto group in the chain. 2-Keto-substituted fatty acids are stable under normal conditions, but when heated with concentrated sulfuric acid they lose carbon dioxide to yield aldehydes. 3-Keto-substituted fatty acids are less stable, losing carbon dioxide, on warming, to yield methyl ketones. 4-Keto-substituted fatty acids, and those with the keto substitution further from the carboxyl group, are as stable as normal fatty acids. 3-Keto acids can partly enolize, but all others are pure keto forms. Diketo acids with the substitution on two adjacent carbon atoms are yellow in color and are obtainable by treating acetylenic fatty acids with concentrated nitric acid.

The most usual method for the synthesis of keto fatty acids is the treatment of acetylenic fatty acids with concentrated sulfuric acid, or other hydrating agents, to add water to the triple bond. Two isomeric keto acids are formed. Robinson has

TABLE I. Hydroxy- and Keto-Substituted Fatty Acids.

Acid	Synonym	Formula	M.p., °C.	Source and ref.
<i>Hydroxy acids</i>				
2-Hydroxy-4,6,6-trimethyl-heptanoic	$\alpha$ -Hydroxydecanoic	$(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CHOHCOOH}$	—	—
(-)-3-Hydroxydecanoic	—	$\text{CH}_3(\text{CH}_2)_8\text{CHOHCH}_2\text{COOH}$	47	<i>Pseudomonas pyocyanus</i> (2)
Sabinic	12-Hydroxydodecanoic; $\lambda$ -hydroxylauric	$\text{CH}_2\text{OH}(\text{CH}_2)_{10}\text{COOH}$	84	<i>Juniperus sabina</i> wax (3)
Juniperic	16-Hydroxyhexadecanoic; $\alpha$ -hydroxypalmitic	$\text{CH}_2\text{OH}(\text{CH}_2)_4\text{COOH}$	95	<i>Juniperus sabina</i> wax (3)
$\iota$ -Hydroxystearic	10-Hydroxyoctadecanoic	$\text{CH}_3(\text{CH}_2)_7\text{CHOH}(\text{CH}_2)_8\text{COOH}$	81-82	(1)
$\lambda$ -Hydroxystearic	12-Hydroxyoctadecanoic	$\text{CH}_3(\text{CH}_2)_9\text{CHOH}(\text{CH}_2)_{10}\text{COOH}$	78-79	(1)
2-Hydroxytetraacosanoic	—	$\text{CH}_3(\text{CH}_2)_{22}\text{CHOHCOOH}$	100	Brain phrenosin (6,10)
Ambrettolic	16-Hydroxy-7-hexadecenoic	$\text{CH}_2\text{OH}(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_8\text{COOH}$	27	Musk oil (9)
Vernolic	10-Hydroxy-8-octadecenoic	$\text{CH}_3(\text{CH}_2)_7\text{CHOHCH}:\text{CH}(\text{CH}_2)_8\text{COOH}$	22	<i>Veronica antheleminica</i> (92% of fat) (13)
Ricinoleic	(+)-12-Hydroxy- <i>cis</i> -9-octadecenoic	$\text{CH}_3(\text{CH}_2)_5\text{CHOHCH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	4-5	Castor oil
<i>DL-erythro-8,11</i> -Dihydroxystearic <sup>c</sup>	<i>DL-erythro</i> -9,10-Dihydroxyoctadecanoic	$\text{CH}_3(\text{CH}_2)_7\text{CHOHCHOH}(\text{CH}_2)_7\text{COOH}$	133	Oleic acid
<i>DL-threo-8,11</i> -Dihydroxystearic <sup>b</sup>	<i>DL-threo</i> -9,10-Dihydroxyoctadecanoic	$\text{CH}_3(\text{CH}_2)_7\text{CHOHCHOH}(\text{CH}_2)_7\text{COOH}$	99	Soils and straw
11,12-Dihydroxyeicosanoic	—	$\text{CH}_3(\text{CH}_2)_7\text{CHOHCHOH}(\text{CH}_2)_8\text{COOH}$	130	Hare's-ear-mustard-seed oil (8)
Lanoceric	?-Dihydroxytriacontanoic	$\text{C}_{30}\text{H}_{60}\text{O}_4$	104-105	Wool wax

Acid	Synonym	Formula	M.p., °C.	Source and ref.
$\beta$ -Aleuritic	$\beta$ -9,10,16-Trihydroxyhexadecanoic; <i>erythro</i> - $\theta$ , $\iota$ , $\alpha$ -tri-hydroxypalmitic <sup>a</sup>	$\text{CH}_2\text{OH}(\text{CH}_2)_3\text{CHOHCHOH}(\text{CH}_2)_7\text{COOH}$	104	Shellac
$\alpha$ -Sativic	?-Tetrahydroxystearic	$\text{C}_{18}\text{H}_{36}\text{O}_6$	174	Oxidation of linoleic acids
$\beta$ -Sativic	?-Tetrahydroxystearic	$\text{C}_{18}\text{H}_{36}\text{O}_6$	163.5	Oxidation of linoleic acids
<i>Keto acids</i>				
Pyruvic	2-Oxopropanoic; $\alpha$ -ketopropionic	$\text{CH}_3\text{COCOOH}$	3	Intermediate catabolism of sugars and fats
Acetoacetic	3-Oxobutanoic; $\beta$ -ketobutyric	$\text{CH}_3\text{COCOCH}_2\text{COOH}$	—	Intermediate catabolism of fats
$\gamma$ -Ketostearic	4-Oxo-octadecanoic	$\text{CH}_3(\text{CH}_2)_{13}\text{CO}(\text{CH}_2)_2\text{COOH}$	96	(1)
$\epsilon$ -Ketostearic	6-Oxo-octadecanoic	$\text{CH}_3(\text{CH}_2)_{11}\text{CO}(\text{CH}_2)_4\text{COOH}$	87	<i>Lactarius</i> fungus (1)
$\iota$ -Ketostearic	10-Oxo-octadecanoic	$\text{CH}_3(\text{CH}_2)_7\text{CO}(\text{CH}_2)_8\text{COOH}$	82.4	(1)
$\pi$ -Ketostearic	17-Oxo-octadecanoic	$\text{CH}_3\text{CO}(\text{CH}_2)_{15}\text{COOH}$	88.6	(1)
13-Oxodotriacontanoic	—	$\text{CH}_3(\text{CH}_2)_{18}\text{CO}(\text{CH}_2)_{11}\text{COOH}$	105	Cochineal wax (5)
13-Oxohexatetracontanoic	—	$\text{CH}_3(\text{CH}_2)_{22}\text{CO}(\text{CH}_2)_{11}\text{COOH}$	115	(12)
$\alpha$ -Licanic	4-Oxo-9,11,13-octadecatrienoic	$\text{CH}_3(\text{CH}_2)_3(\text{CH}:\text{CH})(\text{CH}_2)_4\text{CO}(\text{CH}_2)_2\text{COOH}$	74-75	Oiticica oil
$\epsilon$ , $\delta$ -Diketostearic	6,7-Dioxooctadecanoic	$\text{CH}_3(\text{CH}_2)_{10}\text{COCO}(\text{CH}_2)_4\text{COOH}$	86	—
$\theta$ , $\iota$ -Diketostearic	9,10-Dioxooctadecanoic	$\text{CH}_3(\text{CH}_2)_7\text{COCO}(\text{CH}_2)_7\text{COOH}$	98	—

<sup>a</sup> *erythro*- denotes a configuration similar to the sugar erythrose.<sup>b</sup> *three*- denotes a configuration similar to the sugar threose.



elaborated general methods for synthesizing higher keto acids (12). Bergström has synthesized all the possible monoketostearic acids (1).

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F. L. BREUSCH

### Ricinoleic Acid, $C_{18}H_{34}O_2$ .

Ricinoleic acid (ricinolic acid), formula weight 298.46, comprises about 86% of the fatty acids in castor oil (*q.v.*). Ricinoleic acid was first isolated and named by Saal-müller a hundred years ago, and Goldsobel established the structure as 12-hydroxy-9-octadecenoic acid. Of the two possible geometric isomers, ricinoleic acid is the *cis* form, m.p. 4-5°C.; the *trans* isomer, m.p. 52-53°C., called ricinelaidic acid by Krafft, is not present in castor oil, but can be readily produced from ricinoleic acid by treatment with nitrogen oxides.

Pure ricinoleic acid has never been obtained from castor-oil fatty acids; ricinoleic acid of 96.5% purity has been prepared by crystallization of the fatty acids with acetone at -70°C. Commercially, ricinoleic acid is never isolated from the crude fatty acids of castor oil, which are used as such in manufacturing derivatives of ricinoleic acid. In commercial terminology, "ricinoleic acid" means the fatty acids (castor fatty acids) obtained by splitting castor oil hydrolytically and the derivatives are commonly called ricinoleates.

This acid and licanic acid (see p. 295) are unique among the fatty acids occurring naturally to any considerable extent in that they have three different functional groups: ricinoleic acid contains the hydroxyl group, the carboxyl group, and the double bond. It is the hydroxyl group that is chiefly responsible for the commercial importance of castor fatty acids. These acids and their derivatives are used in the manufacture of surface-active agents, plasticizers, and lubricating-oil additives, as well as for the production of chemicals, such as sebacic acid, methyl *n*-hexyl ketone, capryl alcohol, 10-undecylenic acid, and heptaldehyde.

### PHYSICAL AND CHEMICAL PROPERTIES

Some constants of castor fatty acids and of ricinoleic acid are shown in Table II. Pure ricinoleic acid is dimorphous. When the specifically purified acid is not too strongly supercooled, it solidifies very slowly and melts at 6-8°C. However, if the liquid acid is kept for a long time at 7°C., the crystals obtained melt at 15-17°C. If

TABLE II. Some Constants of Castor Fatty Acids and of Ricinoleic Acid.<sup>a</sup>

Acids	M.p., °C.	$d_{4}^{15.5}$	$n_D^{20}$	Iodine value (Wijs)	Neutralization value	Acetyl value <sup>b</sup>
Castor-oil. . . . .	13	0.957-0.967	1.4546	87-93	182-193	146-150
Ricinoleic. . . . .	4-5	0.940	1.4716	88.5	187.98	137.9

<sup>a</sup> Analytical methods, unless otherwise noted, are those of A.S.T.M. D555-47.

<sup>b</sup> American Oil Chemists' Society method.

the melt of the latter form is rapidly crystallized by cooling suddenly to  $-30^{\circ}\text{C}.$ , the melting point remains unchanged. However, if this melt is kept for several hours at  $4-5^{\circ}\text{C}.$ , and then solidified by moderate cooling, the low-melting form is again obtained (6).

Ricinoleic acid was found by Walden to exhibit a specific rotation of from  $+6.25$  to  $+7.5^{\circ}$ , due to the asymmetry of carbon atom 12, which bears the hydroxyl radical. Ricinelaidic acid similarly exhibits a specific rotation of  $+6.67^{\circ}$ . The levorotatory optical isomers of these two acids have not been found in nature nor have they been produced in the laboratory.

Pure ricinoleic acid, as well as castor fatty acids, is miscible with alcohol and ether in every proportion. Even at 15 mm. Hg, it cannot be distilled without decomposition.

#### MANUFACTURE OF CASTOR FATTY ACIDS

Castor fatty acids are produced by heating batches of castor oil with excess aqueous caustic soda solution. The soap formed is then split with dilute hydrochloric acid rather than with sulfuric acid. This produces better-quality acids. The upper layer is separated from the aqueous layer and allowed to drain as free of moisture as possible.

If the fatty acids are to be stored for any length of time, it is better to leave them slightly alkaline by using less than the theoretical amount of acid. If the small amount of soap remaining interferes with any future processing, the rest of the mineral acid should be added at the time of use. If the acids are not left slightly alkaline, they are likely to form polyricinoleic acid in storage. The polymerized acid can be reconverted with difficulty into the original acid by saponification with alcoholic potassium hydroxide and decomposition of the soap formed with hydrochloric acid.

During 1948, approximately 3300 tons of No. 3 castor oil was hydrolyzed to castor fatty acids. This represented 35% of the production of this grade of castor oil or 15% of the total castor-oil production (grades No. 1 and No. 3).

#### PRODUCTS DERIVED FROM RICINOLEIC ACID OR CASTOR OIL

**Soaps.** The sodium and potassium soaps of castor fatty acids are used commercially (see Vol. 3, p. 244). The alkaline earth and heavy-metal soaps of castor fatty acids, known as ricinoleates, are not used in large volume industrially (see *Driers and metallic soaps*).

**Sulfated Products.** The sulfation of castor oil (see Vol. 3, p. 240) and of castor fatty acids is very similar. The fatty acids and their esters are sulfated by running 15-30% excess sulfuric acid, chlorosulfonic acid, or oleum into the fatty material at  $20-35^{\circ}\text{C}.$  Since the mixture of fatty acids and sulfating agent tends to become viscous, solvents may be used to keep the mass more fluid. The sulfation reaction is allowed to proceed for one or more hours depending on the degree of sulfation desired.

The sulfated mass is then washed with water or salt solution and neutralized with alkali. Sufficient alkali is added not only to neutralize the sulfate group, but also a portion of the carboxyl groups. The amount of alkali added or the degree of neutralization of the carboxyl group depends upon the ultimate use of the sulfated fatty acids. The properties of the sulfate depend not only on the amount of sulfation, but also on the degree of neutralization or the amount of free organic acidity.

Sulfation occurs at the hydroxyl group rather than at the double bond under the above conditions. If sulfation at the double bond is desired, the reaction is run at temperatures of from  $-5$  to  $+10^{\circ}\text{C}$ . Otherwise, the processing does not differ from the procedure previously described.

These sulfated products are used as emulsifiers, dispersing agents, and other surface-active agents, and in the textile industry as aids in the dyeing and finishing of fabrics.

**Esters.** Ricinoleic acid can be esterified on the carboxyl group, the hydroxyl group, or on both, or by self-esterification (polymerization).

*Esters on the Carboxyl Group.* Alkyl esters of ricinoleic acid are prepared by most of the standard methods of direct esterification. Care must be taken, however, to see that polymeric intramolecular esters are not formed. Commercially, this is accomplished by the use of a larger excess of alcohol than is normally used in the esterification of fatty acids. The major portion of the alkyl esters of castor fatty acids produced commercially is manufactured by the alcoholysis of castor oil with alkaline catalysts. This avoids the difficulties encountered in direct esterification. See also "Ester-alcohol interchange" under *Ester interchange*.

Properties of some of the alkyl esters of purified ricinoleic acid are shown in Table III.

TABLE III. Properties of Purified Alkyl Ricinoleates.

Alkyl	M.p., $^{\circ}\text{C}$ .	$t_{13}$ , $^{\circ}\text{C}$ .	$d_4^{22}$	$n_D^{22}$	$[\alpha]_D^{22}$
Methyl.....	$-4.5$	$245_{10}$	0.9236	1.4628 <sup>20</sup>	$+5.19^{27}$
Ethyl.....	—	258	0.9145	1.4618	$+5.28$
<i>n</i> -Propyl.....	—	268	0.9079	1.4573	$+4.15$
Isopropyl.....	—	$260_{10}$	0.9083	1.4583	$+4.04$
<i>n</i> -Butyl.....	—	275	0.9058	1.4566	$+3.73$
Isobutyl.....	—	$262_0$	0.9028	1.4538	$+4.01$

The lower alkyl esters of castor fatty acids are useful as solvent-type plasticizers, especially for cellulose and cellulose-derived polymers (7,15). The partial esters of castor fatty acids with glycerol, ethylene glycol, propylene glycol, diethylene glycol, and higher polyethylene glycols are used in various cosmetic creams and ointments, as well as for emulsifiers and dispersing agents (3).

*Esters on the Hydroxyl Group.* Acyl esters of ricinoleic acid or of castor fatty acids can be prepared by treating the acids with the appropriate acid anhydride or acid chloride by conventional methods. Only the acetyl derivatives of the acids have been reported. These products are of little commercial importance.

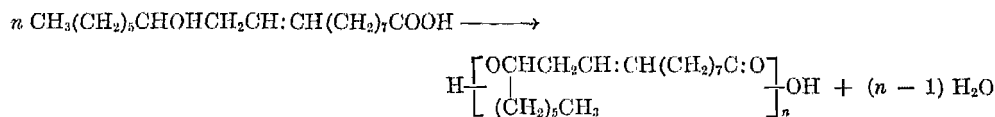
*Esters on Both the Carboxyl and Hydroxyl Groups.* Mixed alkyl and acyl esters are usually produced by treating alkyl esters with the appropriate acid anhydride or acid chloride. Some of the properties of the purified esters of this type that have been prepared are shown in Table IV.

TABLE IV. Properties of Alkyl Esters of Purified Acylated Ricinoleic Acids.

Alkyl	Acyl	$b_{15}, ^\circ\text{C.}$	$d_4^{25}$	$n_D^{25}$	$[\alpha]_D^{25}$
Methyl	Acetyl	170 <sub>0.1</sub>	0.9353	1.4570	+15.25
Methyl	Propionyl	260	0.9226 <sup>18</sup>	1.4535 <sup>18</sup>	+16.88 <sup>18</sup>
Methyl	Benzoyl	195-196 <sub>0.08</sub>	—	—	—
Ethyl	Acetyl	257	0.917	1.4540	+14.85
Ethyl	Propionyl	265	0.915 <sup>18</sup>	1.4517 <sup>18</sup>	+16.06 <sup>18</sup>
<i>n</i> -Propyl	Acetyl	260	0.912	1.4513	+14.40
<i>n</i> -Propyl	Propionyl	315 <sub>0.45</sub>	0.913	1.4498	+13.61
<i>n</i> -Butyl	Acetyl	243 <sub>18</sub>	—	—	—
Isobutyl	Acetyl	257	0.912	1.4548	+9.58
Isobutyl	Propionyl	330 <sub>0.10</sub>	0.903	1.4245	+9.25

Although the alkyl esters of castor fatty acids are effective solvent-type plasticizers for cellulosic polymers, the alkyl acyl esters are compatible and effective with a greater variety of polymers. However, esters of this general type, for example, methyl acetyl ricinoleate (methyl ricinoleate acetate), have only limited compatibility with polyvinyl chloride resins (1). The acetylated castor esters of ethylene glycol monoaryl or monoalkyl ethers are also valuable plasticizers (10).

*Polymeric or Self-Esters of Ricinoleic Acid.* Since ricinoleic acid is a hydroxy acid, the carboxyl group of one molecule can esterify the hydroxyl group of a second molecule and so on. This esterification is readily carried out by moderate heating and can be represented by the following equation:



where  $n$  ranges from about 4 to 10. This reaction leads to the formation of a low-molecular polymeric ester known as polycinoleic acid, which is a viscous oil. It can be esterified with various alcohols and acylated with acid anhydrides or acid chlorides by conventional methods to yield alkyl esters, acyl esters, or alkyl esters of the acylated polymeric ester. Esterification occurs because, due to the low molecular weight of the polymer, there are still a large number of hydroxyl and carboxyl groups available for further reaction. The methyl, ethyl, and butyl esters of acetylated polycinoleic acid are good plasticizers. They offer the advantage over the corresponding derivatives of the unpolymerized acid that the volatility is considerably lower.

**Hydrogenation Products.** The olefin linkage present in the alkyl esters of ricinoleic acid can be hydrogenated in the presence of nickel catalysts at 130-150°C. (see Vol. 3, p. 243). The products are the corresponding alkyl esters of 12-hydroxystearic acid. By the use of a cobalt catalyst or of various metal chromites (for example, copper), alkyl ricinoleates or castor oil can be reduced to 1,12-octadecanediol at temperatures above 200°C. This involves the addition of hydrogen to the double bond and reduction of the ester group to a primary alcohol.

Alkyl ricinoleates or castor oil can be rearranged to alkyl 12-ketostearates or 12-ketostearin, respectively, by heating under hydrogenation conditions in the presence of cobalt or nickel catalysts. This rearrangement involves a simultaneous dehydrogenation of the secondary alcohol group and hydrogenation of the double bond (11).

By sodium and alcohol reduction, which has been applied economically to the hydrogenation of oils (4), ricinoleyl alcohol (1,12-octadecenediol) has been produced from methyl ricinoleate and from castor oil.

12-Hydroxystearic acid and its esters are used in cosmetics, ointments, synthetic waxes, and as mold-release agents.

**Oxidation Products.** Both azelaic and suberic acids can be produced from the ricinoleic acid in castor fatty acids by treatment with nitric acid (8) (see Vol. 1, pp. 154-55).

**Degradation Products.** Castor oil, the esters of castor fatty acids, or preferably the sodium soaps are degraded by strong caustic soda to yield sebacic acid and a mixture consisting of methyl *n*-hexyl ketone and capryl alcohol (2-octanol).

**Products of Pyrolysis.** Castor oil can be thermally decomposed to yield acrolein, heptaldehyde (enantaldehyde), undecylenic acid (see p. 266), and a residue. The residue is difficult to remove from the reactor owing to its high viscosity and low solubility in the usual solvents. This difficulty has been partially overcome by the addition of materials such as ester gum to the charge. If an ester or an amide of castor fatty acids is used as the starting material, the products are the undecylenic ester or amide, respectively, as well as heptaldehyde (12,13,14).

Temperatures of 300-550°C. have been reported for the pyrolysis. It has been shown that below 425°C. the chief reaction is the decomposition of the glycerol portion of the castor oil to yield acrolein and water by dehydration and rearrangement (5,9). Above 465°C., the desired cleavage occurs between carbon atoms 11 and 12 to yield heptaldehyde and undecylenic acid. At intermediate temperatures, two side reactions occur. The first involves the self-esterification of the acids to produce polyciclinoleic acid and water. The second involves dehydration to form octadecadienoic acids, which polymerize. The first step of this latter reaction is analogous to the preparation of dehydrated castor oil (see Vol. 3, p. 241); the second step is analogous to the drying of dehydrated castor oil or of linseed oil (see Vol. 5, p. 279). The yield of the desired products can be improved by the use of a vacuum (15-40 mm. Hg) or by the passage of a current of dry superheated steam or other inert gas through the reaction mass.

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**Licanic Acid,  $C_{18}H_{28}O_2$ .**

Licanic acid, formula weight 292.41, contains three conjugated double bonds in the same positions as in eleostearic acid. Licanic acid is a white, crystalline solid, soluble in ethyl alcohol and other organic solvents. Two geometric isomers are known, namely, the  $\alpha$ -acid, m.p. 74–75°C., and the  $\beta$ -acid, m.p. 99.5°C.  $\alpha$ -Licanic acid is the only naturally occurring isomer found in vegetable oils. It composes over 75–80% of the fatty acids of oiticica oil and is an important constituent of oils from po-yoak, behurada, cacahuananche, taritih, *Licania rigida*, *L. crassifolia*, and *Parinarium gladerimum* seed.

$\alpha$ -Licanic acid is unstable and is isomerized to the  $\beta$ -form by sunlight in the presence of traces of iodine or sulfur. Licanic acid and its glycerides readily polymerize upon heating to form gels. Like eleostearic acid, licanic acid readily reacts with two moles of bromine (1) and one mole of thiocyanogen. Licanic acid dissolved in glacial acetic acid, in the presence of a platinum-silica gel catalyst, absorbs three moles of hydrogen and yields hexahydrolicanic acid ( $\gamma$ -ketostearic acid), m.p. 96.5°C.

The  $\alpha$ - and  $\beta$ -isomers of licanic acid yield maleic anhydride adducts, m.p. 79 and 97°C., respectively, which on oxidation with alkaline potassium permanganate yield  $\gamma$ -ketoazelaic and azelaic acids, respectively. On oxidation with neutral dilute potassium permanganate solution at 0°C., licanic acid absorbs 7.3 atoms of oxygen and yields valeric,  $\gamma$ -ketoazelaic, and some oxalic acids, while oxidation with alkaline potassium permanganate yields  $\gamma$ -ketoazelaic acid, valeric acid, and calcium oxalate. Autoxidation of  $\beta$ -licanic acid is accompanied by a decreased spectral absorption in the region of 2600–2800 Å., and increased absorption in the region of 2300 Å. and above 3200 Å.

As ketones,  $\alpha$ - and  $\beta$ -licanic and  $\gamma$ -ketostearic acids yield semicarbazones, m.p. 110–111, 138, and 119°C., respectively.

The esters of licanic acid are less stable than the potassium salt of the acid, but are more stable than the free acid. The methyl ester of licanic acid has the following properties:  $b_D^{20}$ , 242°C.;  $d_4^{15}$ , 0.952;  $n_D^{15}$ , 1.5127; molar refractivity, 96.55; and viscosity at 14°C., 24.5 poises.

Licanic acid is used only in the form of its natural glycerides, that is, oiticica oil, which is the only industrially important oil, at present, containing this acid. Because of the ease of polymerization and other reactions associated with the trienoic conjugation of licanic acid, oiticica oil is used in the protective and decorative-coating industry to produce alkali- and water-resistant films in much the same manner as tung oil (see *Drying oils*).

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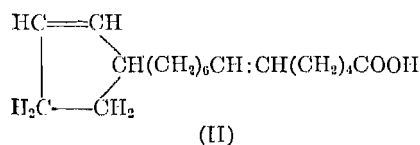
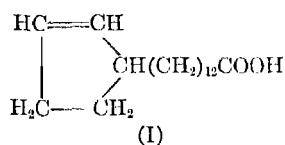
R. S. MCKINNEY

**CHAULMOOGRA-OIL ACIDS**

Chaulmoogra-group oils are obtained from the seeds of certain trees of the order Flacourtiaceae, mostly of the genus *Hydnocarpus* (see Vol. 3, p. 651). The oil from these seeds has been used for centuries in the treatment of leprosy. There appears to be little doubt that the curative powers of these oils are due to the presence of chaul-

moogric acid, its homologs, or related compounds, one or more of which are present as glycerides or free acid in all of the chaulmoogra-group oils. These acids are aliphatic acids characterized by an  $\omega$ -substituted cyclopentenyl group, and contain an even number of carbon atoms from six to eighteen. The highest acid in this homologous series is **chaulmoogric acid** (I),  $C_{18}H_{32}O_2$ . The other members of the series differ from each other by two methylene groups in the aliphatic chain. These acids contain an asymmetric carbon atom and rotate the plane of polarized light strongly to the right. This characteristic is almost unknown among other fatty acids, and hence this property is a very valuable one in determining the presence or absence of the chaulmoogra-oil acids in an oil.

Chaulmoogric acid and the next lower in the series, **hydnocarpic acid**, were first reported in analyses of several chaulmoogra-group oils in 1904 by Power, Gornall, and Barrowcliff (8,9). Other acids in this series of homologous acids are **aleptic**, **alepylic**, **aleprestic**, and **aleprolic acids**, discovered by Cole and Cardoso. Table I lists some of the properties of these acids.



As would be expected, this series of acids shows a regular variation in melting point, optical activity, and iodine number. They range from solid to liquid at ordinary temperature. The higher acids crystallize beautifully, growing upward in branching forms from the melted acid as it solidifies. Even a small amount of impurity inhibits this very characteristic growth, yielding instead a flat upper surface.

One other optically active fatty acid, **gorlic acid**, (II),  $C_{18}H_{30}O_2$ , which does not belong to this homologous series but differs from chaulmoogric acid only in having a double bond in the aliphatic chain, has been reported to be present in several of the oils of the chaulmoogra group (2,4). A "dehydrochaulmoogric acid" reported by Paget in *Carpotroche brasiliensis* oil was undoubtedly the same acid (6). Gorlic acid is a colorless, practically odorless, liquid fatty acid with a high optical activity. It is not as stable as chaulmoogric or hydnocarpic acid.

TABLE I. Some Properties of Optically Active Fatty Acids Found in Chaulmoogra Oils.

Acid	Formula	Formula wt.	M.p., °C.	$[\alpha]_D^{25}$ , degrees	Iodine no.
Chaulmoogric.....	$C_6H_7(\text{CH}_2)_{12}\text{COOH}$	280.2	68.5	+60.3	90.5
Hydnocarpic.....	$C_6H_7(\text{CH}_2)_{10}\text{COOH}$	252.2	60.5	+69.3	100.7
Aleptic.....	$C_5H_7(\text{CH}_2)_8\text{COOH}$	224.2	48.0	+77.1	113.4
Alepylic.....	$C_5H_7(\text{CH}_2)_6\text{COOH}$	196.2	32.0	+90.8	129.7
Aleprestic.....	$C_5H_7(\text{CH}_2)_4\text{COOH}$	168.1	—	+100.5 <sup>a</sup>	151.2
Homolog not found..	$C_5H_7(\text{CH}_2)_2\text{COOH}$	140.1 <sup>a</sup>	—	+110.5 <sup>a</sup>	181.5 <sup>a</sup>
Aleprolic.....	$C_6H_7\text{COOH}$	112.1	—	+120.5 <sup>a</sup>	226.7
Gorlic.....	$C_5H_7(\text{C}_{12}\text{H}_{22})\text{COOH}$	278.2	6.0	+60.7	182.5

<sup>a</sup> Calculated.

Source: reference (4).

The actual isolation of chaulmoogra-oil acids from ordinary fatty acids or from each other cannot be made by the ordinary methods of separation, since they appear in

both liquid and solid acid fractions. Because of this, the physical constants of the pure chaulmoogric and hydnocarpic acids were incorrectly reported in the literature until 1937, when Cole and Cardoso devised a new method for their separation and purification (4). This method was a combination of fractional vacuum distillation of the mixed ethyl esters in a Podbielniak high-temperature fractionating apparatus and fractional crystallization of the free fatty acids prepared from these ester fractions.

The pure ethyl esters are easily prepared from the acids and are fairly stable (4). Some of their properties are given in Table II.

Chaulmoogric acid was first synthesized from simple organic compounds by Perkins in 1927 (7). It was found to be the optically inactive *dl*-form but identical with the natural dextrorotatory substance in other respects. Adams later prepared the dextrorotatory chaulmoogric acid by starting with natural hydnocarpic acid (1).

No large-scale test of the efficacy of the pure chaulmoogra-oil acids or their esters against leprosy has been made, mainly because of the difficulty of preparation. Since gorlic acid contains not only a cyclopentene ring (with one double bond) but also another double bond in the side chain, it has been suggested that its therapeutic effect in leprosy treatment may be greater than that of the other acids.

TABLE II. Some Properties of Ethyl Esters of Optically Active Acids Found in Chaulmoogra Oils.

Ethyl ester	Formula wt.	b <sub>10</sub> , °C.	d <sub>25</sub> <sup>25</sup>	n <sub>D</sub> <sup>25</sup>	[α] <sub>D</sub> <sup>25</sup> , degrees	Iodine no.
Chaulmoograte.....	308.3	222	0.901	1.4592	+55.4	82.5
Hydnocarpate.....	280.2	200	0.907	1.4578	+61.9	90.5
Aleprate.....	252.2	174	0.915	1.4562	+66.5	100.7
Aleprylate.....	224.2	148	0.925	1.4550	+79.1	113.4
Aleprestate.....	196.2	122 <sup>a</sup>	—	1.4538 <sup>a</sup>	+86.5 <sup>a</sup>	129.7
Homolog not found...	168.1	96 <sup>a</sup>	—	1.4526 <sup>a</sup>	+94.1 <sup>a</sup>	151.2 <sup>a</sup>
Aleprolate.....	140.1	70 <sup>a</sup>	—	1.4514 <sup>a</sup>	+101.8 <sup>a</sup>	181.5
Gorlate.....	306.3	232	0.912	1.4667	+55.6	167.0

<sup>a</sup> Calculated.

Source: reference (4), Vol. 61.

A large number of synthetic compounds, some of them similar to chaulmoogric acid, have been synthesized by Adams and co-workers (1,10,11); the majority of these acids were dialkylacetic acids ( $\alpha$ -alkylalkanoic acids) prepared by alkylation of diethyl malonate with appropriate halides. These compounds were tested *in vitro* on leprosy bacillus cultures (10). A clinical test of one of them (ethyl di-*n*-heptylacetate) on 50 patients indicated it was not quite as effective as the *Hydnocarpus wightiana* ethyl esters (5). More recent work with synthetic compounds has indicated that the sulfones are equally or possibly more effective than chaulmoogra preparations in the treatment of leprosy.

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**FD&C DYES.** See *Colors for foods, drugs, and cosmetics.*

## FEEDS, ANIMAL

The term "feed" is used to designate plant and animal products available for livestock consumption, whereas food is the usual term applied to products used for human consumption. Feed consists for the most part of materials that man cannot utilize directly or those that he prefers to have concentrated into a more palatable product. Animal feeding should be regarded as a practice of condensing relatively coarse materials into meat, milk, eggs, wool, or power.

Animal feeds consist largely of plant products, and nearly all pasture and forage are fed to livestock. Whole or ground cereals form a substantial portion of the rations of animals or birds. While feeds may vary in composition because of soil and other environmental conditions, the quantity of the plant material seems to be more easily influenced than the quality (21). According to U.S. Department of Agriculture statistics, of the major cereals, corn leads as a livestock feed; approximately 91% of the crop was fed to livestock in the ten-year period from 1938 to 1947. In addition, approximately 89% of the oats, 69% of the barley, 56% of the grain sorghums, and

**TABLE 1. The Estimated Average Disappearance of Major By-Product Feeds, 1936-45.**

Feed	Amount fed (1000 tons)
Mill products:	
Wheat millfeeds.....	4969
Gluten feed and meal.....	736
Rice millfeeds.....	131
Brewers' dried grains.....	160
Distillers' dried grains.....	300
Dried and molasses beet pulp.....	264
Alfalfa meal.....	618
Oilseed cake and meal:	
Cottonseed.....	1917
Soybean.....	2048
Linseed.....	549
Peanut.....	83
Copra.....	98
Animal proteins:	
Tankage and meat scraps.....	766
Fish meal.....	224
Dried milk.....	119

11% of the wheat were used as feed. In addition to the enormous quantity of cereals fed before technological processing, a very substantial tonnage of by-products from industrially processed cereals is also fed to livestock. The approximate tonnages of the more common by-product feeds fed to livestock are given in Table I (from *Agricultural Statistics—1947*).

Detailed analyses of various livestock feeds and their digestibility coefficients and total digestible nutrient values have been summarized by Morrison (15) and others (7,16). The analyses of some of the more common by-products used in feeds are given in Table II (7). Seldom does one feed make up the sole ration of an animal. Feeding standards have been prepared to aid in compounding rations suitable for various levels of production, and the most commonly used of these is the Morrison standard (15).

TABLE II. The Approximate Chemical Composition of Some Common By-Product Feeds and the Parent Seed.

Feedstuff	Moisture, %	Ash, %	Crude protein, %	Ether extract, %	Crude fiber, %	Nitrogen- free extract, %	Calcium, %	Phosphorus, %
Barley	9.6	2.9	12.8	2.3	5.5	66.9	0.07	0.32
Brewers' dried grains:								
18-23% protein	7.9	4.1	20.7	7.2	17.6	42.5	0.16	0.47
23-28% protein	7.7	4.3	25.4	6.3	16.0	40.3	0.16	0.47
Copra meal, new process	8.9	6.6	21.4	2.4	13.3	47.4	0.28	0.58
Corn, shelled	12.9	1.3	9.3	4.3	1.9	70.3	0.01	0.26
Corn gluten meal	8.0	2.2	43.0	2.7	3.7	40.4	0.10	0.47
Cottonseed meal, 38- 43% protein	7.3	6.1	41.0	6.5	11.9	27.2	0.19	1.11
Distillers' dried grain (corn)	7.0	2.4	28.3	9.4	14.6	38.3	0.04	0.29
Linseed meal, 33-38% protein	8.5	5.6	35.3	5.4	8.3	36.9	0.36	0.84
Milo	9.3	1.6	12.5	3.2	1.5	71.9	—	—
Molasses, cane	24.0	6.8	3.1	—	—	66.1	0.35	0.06
Oats	7.7	3.5	12.5	4.4	11.2	60.7	0.10	0.40
Oat groats, ground rolled	10.4	2.6	17.3	6.6	1.8	61.3	0.08	0.43
Oat hulls	5.8	6.5	4.3	1.9	30.8	50.7	0.09	0.12
Peanut meal, 38-43% protein	6.4	4.4	41.6	7.2	16.0	24.4	0.10	0.50
Rice bran	8.8	12.2	12.8	13.8	12.2	40.2	0.10	1.84
Rice hulls	6.5	21.9	2.1	0.4	44.8	24.3	0.08	0.06
Soybean meal, 38-43% protein	7.8	5.8	41.7	5.8	6.2	32.7	0.29	0.67
Wheat	10.6	1.8	12.0	2.0	2.0	71.6	0.05	0.38
Wheat bran	9.4	6.4	16.4	4.4	9.9	53.5	0.10	1.14
Wheat, brown shorts	10.8	4.0	17.8	4.8	5.8	56.8	0.08	0.86

### Cereals and Their By-Products

In general, the cereals (*q.v.*) and their by-products are very palatable to livestock, but, because of their relatively high price, the quantity used is often restricted (except in feeding swine) to that amount that gives optimum economy of production. This class of feeds represents a high concentration of energy, but the cereals as individual

grains are often lacking in both quantity and quality of protein or in the proper proportion of the so-called essential amino acids (14,15,19). Cereal by-products often have a high protein concentration, but are usually deficient in the quality of protein needed for optimum performance when fed as the only supplementary source to poultry and swine.

The cereals are characteristically low in calcium but are a fair source of phosphorus unless produced on soils deficient in the element. Aside from yellow corn, which has an appreciable carotene content, the cereals are low in vitamin A or its precursor carotene. In addition, the cereals are very low in vitamin D. The water-soluble vitamins are much more abundant than the fat-soluble ones. Most of the cereal by-products vary considerably in analysis from the parent grain.

**Barley** is a hard-seeded grain that should be ground, rolled, or crimped for nearly all livestock except sheep; steeped or cooked barley is often used as an appetizer in fitting cattle for exhibition. Nearly all the barley by-products, except those of the brewery industry, result from the manufacture of pearl barley or barley flour for human consumption.

*Barley Feed.* In the manufacture of pearl barley, the hull and outer coats of the kernel are removed in milling and the resulting product is sold as barley feed.

*Barley Mixed Feed.* When barley is processed into flour, the entire offal consisting of barley hulls and barley middlings is sold as the mixed feed. Middlings consist of germ, bran, and coarse flour.

*Barley Hulls.* This product consists of the outer covering of barley after the groats have been removed; sometimes it is mistakenly referred to as barley bran. It is a coarse and bulky feed and should be regarded as a roughage instead of a concentrate.

**Corn** or maize is considered the standard fattening grain for livestock, and most other grains are usually compared with it in experiments comparing different livestock feeds for fattening meat animals (15). In addition, it is widely used in dairy and poultry rations. Corn grain is usually fed as whole-ear corn or shelled corn to hogs, and as shelled grain to sheep, but it is usually ground for cattle past one year of age. When finely ground it is usually called corn meal and when more coarsely divided it is referred to as cracked corn, ground corn, or corn chop. Corn and its by-products are lacking in quality of protein to even a greater extent than most of the other cereals (13).

*Corn bran* consists of the outer coating of the kernel and kernel tip but has very little of the starch or germ.

*Corn Gluten Feed.* In the wet milling of corn starch or for sirup, kernel residues remain that consist of germ, gluten, bran, and corn solubles. A mixture of corn gluten meal and corn bran constitutes a by-product feed sold as corn gluten feed; it may or may not contain corn solubles or corn oil meal. The amount of corn gluten meal is regulated to keep the protein content of the preparation in a range of 25-27%. Gluten feed is fed primarily to dairy cows and is considered most valuable when mixed with more palatable feeds.

*Corn Gluten Meal.* It is a common commercial practice to refrain from mixing corn bran into what would be gluten feed, and the product, containing very little of the outer and coarser part of the corn kernel, is then sold as the gluten meal. Corn solubles and corn oil meal may be mixed into gluten meal. Corn gluten meal has been a common constituent of commercial dairy feeds but is usually not fed as the sole protein supplement. In recent years, the amount of corn gluten meal available for

livestock feeding has been greatly reduced since the meal is used in the production of monosodium glutamate (see Vol. 1, p. 724).

*Corn Oil Cake or Meal.* In the wet milling of corn for the production of corn-starch or corn sirup, the germs are floated from the shredded corn kernels. Pressing the oil from the germs leaves a residue of corn oil cake, but often this is ground and the product sold as corn oil meal. Occasionally germs are separated in the dry-milling process, and, after expressing the oil, the germ cake obtained is usually ground to corn germ meal.

*Hominy Feed.* When hominy grits, pearl hominy, or corn meal is prepared for human consumption, the corn bran, germ, and a portion of the starch are removed from the kernel by dry milling, and the mixture is sold as hominy feed. The product sold must contain at least 5% fat (1). In composition and feeding value, it closely resembles the corn grain from which it originates.

The **grain sorghums** consist principally of the milos and kaffirs and are grown extensively in the great high plains area east of the Rocky Mountains. In recent years, dwarf or "combine" types of plant growth that lend themselves to mechanical harvesting have been introduced. In composition and feeding value the various sorghum grains resemble corn; usually the grain is fed as ground or chopped grain to cattle and hogs, but is fed whole to sheep. *Grain sorghum gluten feed and meal* are produced in the same manner as the corresponding products are produced from corn. They are not common but are available when corn is comparatively high or scarce, and the grain sorghums are used as a replacement in making alcohol or distilled liquors.

**Oats** are held in very high esteem as livestock feed particularly for dairy cows and growing stock. They are highly palatable, bulky enough to help prevent bolting and overeating, and contain more minerals than the other common feed grains. Oats are usually fed whole to sheep and young cattle but as oat chop or ground oats to other livestock; sometimes, they are crushed or rolled. Oats are too bulky to be used to make up a substantial part of the fattening ration for swine.

*Oat Groats and Oatmeal.* In the process of making oatmeal, the hull is removed and the remaining portion of the kernel is the groat. The broken groats may be rolled, flour resulting from oatmeal manufacture added, and the product sold as "feeding oatmeal." It is considered particularly valuable for starting young chicks or pigs because of its low fiber content which must not exceed 4% (1).

*Oat Hulls.* This product is the outer covering of the oat produced in the milling of oats for their groats. Hulls are extremely bulky, have little nutritive value, and contain so much fiber they should be regarded as a low-grade roughage rather than as a concentrate. Oat hulls are usually sold in mixed feeds and are regarded as an adulterant to the extent that some state feed officials require special labeling when they are used in a mix.

The **rice** produced in the United States is grown in Louisiana, Texas, Arkansas, and California, and most of the grain is processed for human consumption. When the whole grain is cheap or damaged, it may be ground and fed to livestock and as such is called ground rough rice.

*Rice Bran.* When table rice is being milled, the pericarp or bran layer is removed and a certain portion of hull fragments cling to the bran. Rice bran contains over 12% ether extract and hence will turn rancid more rapidly than most other milled products; the product is similar in most other respects to wheat bran, for which it is often used as a substitute in cattle rations.

*Rice Hulls.* These hulls represent the outer covering of rough rice. Although they are fed to livestock and are often included in mixed feeds, such use is not recommended. They are very high in fiber, are quite indigestible, and may cause mechanical injury to the digestive tract. Some states now prohibit their sale in livestock feeds.

*Rice Polish.* In manufacturing table rice the grain is brushed to polish the kernel after the hull and bran have been removed. The refuse thus obtained is high in niacin and thiamine but low in riboflavin and has its highest value in fattening swine (15).

Very little **rye** is used as livestock feed. Its feeding value is low as compared to most of the other farm grains; it lacks in palatability; and its commercial price is usually above its feeding value because of its value in industry, particularly to distilleries. Some rye is milled for household use, and when so processed it yields the same mill products as the other grains milled for flour.

**Wheat** is raised as a grain for human consumption; unless there is an unusual price relationship with the other grains or it is damaged, it is not fed extensively to livestock and poultry. When fed to cattle or hand-fed to hogs, the grain is usually ground, but, when fed to poultry or self-fed to hogs, the whole grain is most commonly used. By-products from the milling of wheat are palatable and valued livestock feeds; many tons of these by-products are incorporated into mixed feeds.

*Wheat bran* is the coarse outer coat of the wheat kernel that has been washed and milled. It is one of the most highly regarded of the mill feeds and is valued for its palatability, bulk, and slightly laxative influence on the animal. Some small mills do not have adequate separation facilities and some flour may be included in the bran; in such case, the product is often referred to as "mill run."

*Wheat-Germ Oil Meal and Cake.* The germs of wheat are pressed to remove a portion of the wheat-germ oil and the resulting cake is available as livestock feed but must contain 29% protein (1); the cake may be ground, and merchandised as meal.

*Wheat Middlings.* Two kinds of wheat middlings are commercially produced, and, of these, the standard middlings contain bran, germ, and some fibrous mill offal but must not contain more than 9.5% crude fiber (1). On the other hand, flour middlings have wheat red dog added to the standard middlings and cannot contain over 6.0% crude fiber (1). Both products are obtained from milling spring wheat.

*Wheat Red Dog.* This product is obtained in regular milling of spring wheat and consists predominantly of aleurone but contains fine bran particles and traces of coarse flour. It must not exceed 4.0% crude fiber (1). It is not usually sold as a separate feed but is more commonly sold in middlings or in mixed feeds. A corresponding product called wheat white shorts is produced from hard red winter wheat.

*Wheat Shorts.* Products corresponding to middlings, both standard and flour, are obtained in milling hard red winter wheat and are called wheat brown shorts and wheat gray shorts, respectively. Both shorts and middlings are valued as hog feeds, particularly by feeders who prefer to feed wet feed or a "slop."

#### CEREAL BY-PRODUCTS

**Brewers' products** are produced by the brewery industry in the malting of grain and in brewing beer (see *Beer and brewing*; *Malt*). Usually, these are fed near the producing plant or are dried and incorporated into mixed feeds.

*Brewers' Grains.* The residue remaining at the close of the malting process is referred to as brewers' grains. Primarily, the product consists of barley that has been

sprouted, the sprouts removed, and the remainder subjected to the enzymic action of diastase (amylase), which changes most of the starch to sugar. Other grains may be added in the manufacture of the wort. Brewers' grains contain approximately 75% water when removed from the vat. They spoil readily if not fed within one or two days. Usually the grains are dried, and the common designation is *brewers' dried grains*.

**Brewers' Dried Yeast.** This is a product obtained by drying the yeast filtered from beer after fermentation is completed, and it must contain 45% protein on a dry-matter basis (1). It is used in poultry and livestock feeds to only a limited extent for its protein content but is often added because it contains a wide variety of the water-soluble vitamins. When irradiated with ultraviolet rays, it is sold as irradiated yeast.

**Malt Sprouts.** This material consists of the sprouts removed from barley sprouted in the malting process. It unavoidably contains hulls, some malt, and other material. The sprouts are dried and usually sold for inclusion in mixed feeds; they must contain a minimum of 24% crude protein (1). In case other grains are malted their sprouts are sold with the prefix name of the grain.

**Distillers' products** are produced when the common cereals are fermented for the production of industrial alcohol or distilled liquors (see *Alcohol, industrial*; *Alcoholic beverages, distilled*).

**Distillers' Dried Grains.** These products are the dried residue obtained by screening the stillage from the manufacture of alcohol and distilled liquors. The name of the grain that predominated in the mixture is prefixed (for example, corn distillers' dried grains). The most common and most valuable of the distillers' grains is produced from corn, and a large part of the production finds its way into dairy-cattle feeds where bulk is not considered undesirable.

**Distillers' Solubles.** Distillers' solubles are obtained by condensing screened stillage from the manufacture of alcohol or distilled liquors. The name prefixed corresponds to the predominating grain. If the product is condensed to a sirupy consistency, it is sold as a semisolid product, or it may be dried and merchandised as the dried product (for example, dried corn distillers' solubles).

**Distillers' Dried Grains with Solubles.** When condensed screened stillage is dried and added to distillers' dried grains, the mixture is sold as containing the solubles. The latter product is rich in the water-soluble vitamins and makes the feed more valuable in poultry feeding but does not materially improve it for sheep or cattle. If the product is not dried, it can be sold in a sirupy condition as semisolid distillers' dried grains with solubles.

### Oil-Bearing Seeds and Their By-Products

Oil-bearing seeds are not commonly fed whole to livestock although most of them can be safely fed as protein supplements. Occasionally, there is some objection to them as feeds because of their high oil content, but the chief objection to feeding them whole is that the oil is too valuable commercially. The high protein residue remaining after expressing the oil is used extensively to supply needed protein to livestock and poultry rations. Proteins obtained from oilseeds are usually not as well balanced in amino acid content as those obtained from animal sources; hence oilseeds should not be the chief source of protein for animals critical to protein quality (13,15). See *Fats and fatty oils*.

**Cottonseed** (*q.v.*) can be fed as a protein supplement, but usually the price of

cottonseed oil makes this practice unwise. Occasionally the whole seed with hull attached is pressed without cooking to remove the oil and the residue sold as whole pressed cottonseed.

**Cottonseed Meal and Cake.** Each ton of cottonseed yields approximately 950 lb. of cottonseed meal or cake, and it is sold on a guaranteed protein content, most commonly 41% crude protein. After the hulls are removed by mechanical separation, the seed is treated by the hydraulic expeller, or solvent methods to remove most of the oil (see Vol. 4, pp. 584-85). Pressure meals usually contain more than 6% ether extract while the solvent production has less than one-half that amount. Solvent meals are not as palatable but have been shown to be as useful in balancing the rations of cattle (8). Cottonseed meals vary not only in method of preparation, but also in the amount of hull remaining with the seed. In commercial practice, the meals or cake are sold subject to well-defined sizes and quality grades (1). Under most economic conditions, cottonseed meal or cake is fed in amounts only adequate to balance the rations of fattening cattle or dairy cattle, but when cheaper than grain it may be fed to replace corn grain, pound for pound (15,17). Usually cottonseed meal is not considered safe for hogs in excess of 10% of the ration because of its possible gossypol content (15). When manufacturers include enough hull in cottonseed meal to exceed the allowable crude fiber limits specified by respective state feed control officials, the product is marked as cottonseed feed at a stipulated protein content.

**Cottonseed Hulls.** The mechanically removed cottonseed hull is a low-protein roughage not unlike other nonlegume roughages. It is usually used to replace hay in the ration, partially or entirely, and is particularly useful when concentrates are to be mixed into and fed with the roughage as a complete ration for ruminants.

**Linseed and Flax Products.** Flax is grown principally in the North Central States, and the two principal uses of the crop are to produce linseed oil, widely used in paint, and linseed meal, valued as a protein supplement for livestock.

**Linseed Meal and Cake.** The oil may be removed from flaxseed by the same methods as cottonseed oil, but most of it is obtained by the hydraulic process, commonly called "old process," and this produces linseed meal or cake. When flaxseed is extracted by solvents, the resulting cake or meal is called "new process"; this procedure results in a less palatable product and one that has less favor with feeders. Linseed cake is graded into various sizes, and when ground it is called meal and as such is most usually fed to livestock. Linseed meal and cake are particularly valued by cattle feeders because these products produce a gloss in the coat of the animal that results in sales appeal at market. In addition, these feeds are very palatable and are good appetizers in cattle rations.

**Peanut Products** (see *Nuts*). The product resulting from the extraction of a portion of the oil from peanut kernels is *peanut oil meal or cake*. It is produced, sold, and used in a manner similar to cottonseed meal. *Unhulled peanut oil feed* is the name for the residue left after oil is extracted from the whole unshelled peanut.

The **soybean** (*q.v.*) has played an important role in livestock feeding only since about 1920. Today it is a widely used source of protein supplements for livestock feeding, and these supplements are considered to be among the best-quality proteins available from plant sources. Since soybeans are competitive acreage with corn as a cash crop, the supply of soya products is dependent upon the price of soybean oil. The whole beans can be ground and fed as a protein supplement, and they are so used when the price of oil does not justify the sale of beans and the purchase of meal.



Usually this is an economic waste and is avoided. Feeding beans to swine may result in soft or oily pork because the melting point of the pork fat is raised by the high melting point of the ingested oil.

*Soybean Oil Meal and Cake.* These products are, in general, produced like the cottonseed products, but a much higher per cent of the total production is by the solvent method because the ether extract content can be reduced to less than 1.0% as compared to more than 5% for the pressure-produced meals. Nearly all the increase in production facilities since 1940 has been for the production of solvent meal, and as worn-out equipment is replaced, extraction methods are being installed. Solvent meals are satisfactory as protein supplements for cattle and sheep (8) and can be used as satisfactorily for poultry and swine as the pressure-produced meals if the meal is heated sufficiently to make the cystine and possibly other essential amino acids available. Most pressure meals exceed 41% in crude protein content while solvent meals may exceed 45% crude protein.

*Other Oil Feeds. Coconut (Copra) Oil Meal or Cake.* Coconut meal or, as it is sometimes called, copra meal is obtained by extracting part of the oil from the dried meat of the coconut. Its preparation is similar to that of the other oilseed meals, but it usually contains only about 21% protein; little of it is sold through retail channels since most of the production is included in mixed feeds.

*Palm-Kernel Oil Meal.* This is a low-protein meal, containing less than 20% crude protein, that represents the residue when palm oil is extracted from the kernel by pressure or solvents.

*Sesame Oil Meal.* A product very similar in composition and feeding value to cottonseed meal is obtained when most of the oil is removed from the sesame seed.

### Forages and Their By-Products

Few forages are processed commercially and hence they are not an important item in manufacturing. However, they are extremely important as livestock feeds and form a most important part of the rations of growing and mature ruminants. Even the simple-stomached animals can make excellent use of certain types of forage.

**Alfalfa** is the forage crop that most commonly becomes an item of commerce after it is processed. If merely chopped before sale it is sold as chopped alfalfa. Occasionally chopped alfalfa hay or chopped stems are treated with blackstrap or other molasses and sold to cattle feeders for their appetizing value.

*Alfalfa Meal.* This product is obtained by grinding alfalfa hay into meal, but it must not contain more than 33% crude fiber (1); hence most of the leaves must be present. Alfalfa meal may be made from sun-cured hay or from alfalfa that is dried by artificial heat in a rotary dryer. The latter method preserves carotene but produces a product with lower vitamin D potency. Feed manufacturers like to obtain meals high in carotene, but the carotene content declines with storage. Artificially dried meals may exceed 175 p.p.m. of carotene when first made, but lower values are more common. Most alfalfa meals are used in mixed feeds because of their value in correcting common nutritive deficiencies.

*Alfalfa Leaf Meal.* When the leaves of alfalfa are separated and ground, the product is called alfalfa leaf meal providing it contains not less than 20% crude protein and not more than 18% crude fiber. This product is used largely in poultry feeds and in feeds for starting young calves and pigs, where the maximum corrective properties

of alfalfa are desired and yet the fiber content of the ration needs to be held at a minimum.

*Alfalfa stem meal* represents the ground residue from the production of alfalfa leaf meal. It is coarse, of low feeding value, and valued mostly as a carrier for liquid feeds such as molasses.

*Lespedeza products* are similar in major aspects to alfalfa products but are much less commonly produced.

*Straw Meal.* Any ground residue that remains after seed is separated from the mature plants may be marketed as straw meal, providing the originating plant name is used as a prefix. Its presence in a feed should be regarded as a filler.

### Animal By-Products

The various animal by-products are almost without exception highly desirable feeds and as a result are relatively scarce and high in price. Thus, they are used almost exclusively for those animals and poultry that are considered most critical in their requirements, or where high levels of digestibility and assimilation are essential. While animal by-products were first used to supply protein in the ration, they have been found to be excellent sources of preventive and corrective nutrients. Their use is not necessarily indicated for grown animals or species that are not critical in their requirements.

**Milk** (see *Dairy products*) is considered the near perfect food for growing young. Its principal dietary deficiency is iron but it contains an abundance of nearly all other required nutrients (13). The value of cows' milk for human food precludes its use for nearly all livestock except nursing young. Milk products that enter directly into commerce originate from creameries and processing plants that obtain cream or whole milk from producers. Farms that sell cream use skim milk, resulting from centrifugal separation, as feed for growing calves, poultry, and swine to supply partially or entirely the supplementary protein needed to balance a diet that contains low-protein cereals. Only small amounts of skim milk from processing plants are available as livestock feed, because it can be more advantageously sold for human consumption. Dried milk products contain only 8% or less water.

**Buttermilk and Its Derivatives.** Buttermilk is the watery residue that remains after butter has been removed from the churn. Unless water has been added in excess, it has a similar composition and feeding value to skim milk. It is too bulky for transportation and hence is usually sold as the dried or condensed product. It must not contain more than 8% water or more than 13% mineral matter (1). It is especially used in poultry mixed feeds and for preparing feeds for young calves and pigs. In manufacturing evaporated or condensed buttermilk, water is removed until the product contains at least 27% total solids and a minimum of 0.055% butterfat and a maximum of 0.14% for each per cent of solids (1). The condensed or semisolid products are most widely used in poultry and swine feeding where maximum feed consumption and performance are of greater importance than economy.

**Casein** (*q.v.*). This is a high-protein product containing at least 80% crude protein that is obtained by the acid or rennet precipitation of skim milk. It is fed only to experimental animals where purity of diet is a consideration.

**Cheese Rind.** In preparing processed cheeses, the rind is removed, cooked, and most of the fat removed. The product is a high-quality meal used like the other animal proteins.

**Skim Milk and Its Derivatives.** Skim milk may be processed and sold similarly to buttermilk, but it is usually merchandised as the dry powder. It may be condensed, or condensed and cultured with suitable bacteria; the cultured product may also be dried. Skim-milk products are sold for the most part for inclusion in commercial poultry feeds where they are particularly valued for their riboflavin content and quality of protein, but a smaller quantity is used in the better grades of calf and pig starters.

**Whey and Its Derivatives.** Whey is the liquid remaining in the cheese vat after the curd has been removed, and it may be dried or condensed in a similar manner to buttermilk and skim milk. The dried product must contain at least 65% lactose (1) and usually contains only about 12% protein. It is even higher in riboflavin than skim milk and is included in mixed feeds as a source of water-soluble fractions.

Enormous tonnages of **packing-house by-products** (see *Meat*) are produced in the processing of meat in modern packing plants, where every effort is made to salvage all that can be utilized from the animal carcass. Some by-products result from the disposal of offal and are often sold below the cost of manufacture to assure sanitary disposal at the least net cost to the plant. Most by-products, however, have sufficient value that often the net profit from such products represents the source of packing-house profits. Efficient by-product production and sales make it possible for the large packer to compete successfully with a local butcher who has lower freight and labor charges.

**Blood Meal.** Packing-house blood (see *Blood, animal*) is collected and heated to produce coagulation, after which moisture is drained and then pressed from the coagulate. After drying, the blood is ground into blood meal. It is a product having usually over 80% protein, but it is not so digestible or high in quality of protein as most of the other animal by-products.

**Bone Meal.** The bones from slaughtered animals are cooked with steam under pressure, and extra fat and protein are removed before the residue is dried and ground to sell as steam bone meal. The bones are sometimes charred in retorts and sold as bone black for clarifying sugar, and, after serving this purpose, they may be recharred and sold as spent bone black for livestock feeding. Bone ash is obtained by burning clean bones without charring.

**Liver Meal.** Most of the wholesome animal liver obtained is sold in the fresh state for human food, but other animal livers are dried and ground into meal which must contain at least 27 mg. of riboflavin per pound (1). Animal liver and glandular meal may be sold but no more than one-half of the material may be of glandular origin, and it must contain 18 mg. riboflavin per pound (1). Liver meal is an excellent source of known and unknown nutritional substances. Numerous workers have reported noticeable response in poultry and young swine when 2% or less of liver meal was added to the ration. The scarcity and high price of such meal prohibits its use merely as a protein supplement.

**Meat Meal or Meat Scraps.** In the preparation of meat meal or scraps, animal tissue exclusive of hair, horn, hoof, and blood is dry-rendered in an open kettle heated by steam. The excess water is driven off, the fat removed, and the residue dried and ground. The product usually contains over 50% protein, but, if it contains more than 4.4% phosphorus, it must be labeled as meat and bone meal (or scrap). Although lower in protein than tankage, it is usually preferred by swine and poultry raisers because of its higher quality of protein.

**Tankage.** A product referred to as digester tankage or meat meal tankage is

prepared from the same source of material as meat scraps. The cooking is done under steam in pressure tanks, the fat and liquid are removed, and the residue is pressed to remove additional fat. The liquid is evaporated to form "stick," which is added to the solid residue, and the mixture is dried and ground. Often tankage is standardized to 60% protein by the addition of blood meal. Most tankage is used in swine feeds, but the tonnage produced is declining because of the more efficient methods employed in dry-rendering meat scraps and the higher quality of protein in the resulting product.

### Marine Products

Marine products (see *Fish*; *Fish-liver oils*) have come into much more general use since 1930 than before that date. Some marine by-products are produced when edible fish are processed for human consumption, while other marine products are made by processing inedible fish for feeding purposes (15).

*Condensed Fish Solubles.* Many species of fish are caught for their oil content, and the oil is extracted by hydraulic pressure. Condensation of the water resulting from such pressing produces condensed fish solubles which are regarded as an excellent source of nutrients commonly lacking in the rations of poultry and swine fed in dry lot or under confinement, where green growing plant food is not available.

*Crab Meal.* The undecomposed waste of the crab consisting of shell, viscera, and varying amounts of flesh is ground and dried. The product is high in mineral matter and it must contain at least 25% protein (1). It is not as palatable as most other marine products.

*Fish liver and glandular meal* is a product produced by drying the complete coelomic contents of fish; at least 50% of the dried weight must have originated from fish livers (1).

*Fish Meal.* Fish meal may be produced by drying and grinding undecomposed fish or fish offal from which the oil may or may not have been expressed. In modern practice the excess water is often removed by partial vacuum at lower temperatures than formerly used. This results in a more digestible and higher-quality product. The demand for fish meal has increased rapidly since swine raisers and poultry producers have found it produces excellent growth response when making up only a portion of the supplementary protein requirement. The protein content varies with the source material from which the meal is made.

*Fish Residue Meal.* In the process of manufacturing glue from nonoily fish, a residue remains that can be dried, ground, and sold as fish meal residue. It is a much less common product than fish meal.

*Shrimp Meal.* Shrimp meal may consist of ground dried shrimp waste, such as the head and hull, and may or may not contain whole shrimp. Shrimp meal often contains less than 40% protein but can replace fish meal if enough more is fed to supply the same protein intake.

*Whale Meal.* Whale meal can be used to replace other meat meals in livestock feeding if the whale is processed before it starts to decompose. In preparing such meal, the fat is pressed out and the residue dried and ground. The mineral and protein contents depend on the amount of bone in the processed material. Greater care in processing material while fresh would improve the consumer acceptance of the product and provide an increased supply of animal protein suitable for livestock feeding.

### Miscellaneous Feeds

*Beet pulp* (see *Sugar manufacture*) is a residue feed obtained from the sugar beet in the manufacture of beet sugar. It may be fed directly as it comes from the plant, as wet beet pulp, or it may be ensiled and fed as beet pulp silage. If the product is to be shipped, it is dried and sold as dried beet pulp or dried and mixed with molasses and called dried molasses beet pulp. The dried pulps are palatable but bulky, and resemble oats in feeding value except that they contain appreciably less protein and are low in phosphorus.

*Buckwheat Middlings.* In the milling of buckwheat as flour for human consumption such by-products as middlings and hulls are produced which correspond in origin to similar products produced from oats. Middlings are used in preparing dairy feeds but the hulls have little feeding value. The middlings and hulls may be combined and sold as buckwheat feed (1), providing the crude fiber content does not exceed 30%.

*Dried Citrus Pulp.* Citrus pulp is the residue remaining after citrus juice is extracted, and it may or may not contain cull fruit. In some cases, oil is expressed from the peel before it is dried or ground, and the product is then sold as citrus meal.

*Dried Sweet Potatoes.* Before World War II, workers in Alabama (9) and others had shown that sweet potatoes could be fed to livestock, but during the war, interest was renewed in the possibility of using dried sweet potatoes as a carbohydrate concentrate to replace scarce grain in livestock feeding. It was found that they had approximately 90% the value of corn in fattening cattle (3,5). Sweet potatoes may be dried after slicing by spreading in the sun on a suitable slab, or they may be sliced and dried in a drum-type dryer similar to that used for alfalfa and other crops.

*Dried Pomace.* Dried apple and dried tomato pomaces are produced when juice is pressed from the respective fruits. The products are dried and form a satisfactory bulky addition to dairy rations. Either pomace can be fed wet, but as such must be utilized locally.

*Mungbeans.* Mungbeans are a low-fat bean, of oriental origin, used by sprouters to produce commercial bean sprouts for human consumption. Cracked beans or other damaged beans that will not sprout can be ground and fed to beef or dairy cattle to replace other protein supplements (20) for they contain about 25% protein, but they are not very palatable to sheep or hogs.

*Molasses (q.v.).* Three kinds of feeding molasses are available to livestock feeders and feed mixers, but cane or blackstrap molasses is by far the most commonly used. Blackstrap is obtained in the manufacture of cane sugar and is the thick sirupy molasses left after as much sugar as feasible has been crystallized and the excess water removed by evaporation. It must contain at least 48% or more of total sugar expressed as invert sugars (1), and it is a very appetizing and valuable feed when not used in such excessive amounts as to reduce the utilization of other feeds (4). "Feeding beet molasses" is a similar product obtained in the manufacture of beet sugar. "Feeding corn molasses" is obtained in making sugar from corn and must contain 48% or more reducing sugars expressed as dextrose, and must contain at least 60% total carbohydrates (1). Neither is as palatable as blackstrap molasses. Molasses feeds are all low in protein and, when fed beyond their optimum appetizing ability, which is usually not more than 10% of the mix, are less valuable than the common grains because of their lower dry-matter content. When low enough in price, so that extra dry matter can be purchased for less per pound than corn or other grain, molasses feeds

may be used to supply large parts of the concentrate in the ration of beef or dairy cattle.

*Urea (q.v.).* When adequate supplies of naturally occurring proteins are not available or are exceedingly high in price, urea can be fed to ruminants to supply a portion of the nitrogen required, providing readily available carbohydrates are also supplied (6,10,11,12). This synthetic product should not, according to present nutrition knowledge, be used to supply more than 25-30% of the protein of the concentrate and should be thoroughly incorporated in a feed mix.

### Compounded Feeds

The suitability of compounded feeds for various classes of livestock and poultry depends upon the intelligence and integrity used in their processing. Most feed manufacturers attempt to acquaint themselves with problems of nutrition and produce a satisfactory product for the purpose intended. The economy of a livestock or poultry feeder using compounded feeds will depend upon the ability of the manufacturer to supply him with as good a feed at the same or less cost than he can obtain by compounding his own rations. Often, especially in the case of poultry feeds, the high price and difficulty experienced in obtaining expensive ingredients that may be needed in small quantities indicate the use of a factory-prepared product.

It is much easier for a feed mixer to add small amounts of certain substances to a mixed feed than it is for the feeder to incorporate such in the ration. Some nutrients are required in larger amounts for some animals or birds than for others, and the mixer can consider these requirements in compounding rations. Choline, for instance, has been shown to be required in relatively larger amounts in chick and poultry rations to prevent perosis in the growing chick and to prevent mortality and low hatchability in hens. Some feeds suitable in most respects for poultry or other critical animals may or may not be good sources of choline and other known nutritional substances (15), and these may be added if the total ration lacks the amount required to adequately nourish the animal or bird. In recent years a substance called the "animal protein factor" (APF) has been found to have great value when added to certain feeds or combinations of feeds. The factor is now added as routine mixing procedure by some feed manufacturers in preparing certain chick and pig rations to insure the presence of enough of the substance for optimum growth.

The discovery of the animal protein factor and its inclusion in livestock feeds is an outgrowth of studies with the antipernicious-anemia factor found in liver and of the discovery that this factor gave unusual response when added to the rations of chicks, rats, and swine supplemented only with vegetable proteins. Subsequent crystallization of the active liver substance followed, and it was referred to as vitamin B<sub>12</sub> (see *Vitamins*). Crystalline B<sub>12</sub> produces many of the characteristic responses of the animal protein factor when fed to birds and pigs, but many workers feel the latter factor has at least one and possibly other unidentified fractions. Vitamin B<sub>12</sub> is produced in the production of the antibiotics streptomycin (*q.v.*) and aureomycin by mold fermentation with cultures of *Streptomyces griseus* and *S. aureofaciens*. Commercial APF is a residue from such production and contains the crystalline vitamin and usually antibiotics. Vitamin B<sub>12</sub> is a nutritional factor which is absolutely essential for normal growth, whereas the role of the antibiotics has not been elucidated and probably varies with the ration and environment. Present data indicate that 50

micrograms of vitamin B<sub>12</sub> per kilogram of dry matter is adequate for the pig (17), while 30 micrograms per kilogram of ration is ample for the chick (18).

Commercial feeds are usually prepared under "closed" formulas but may be sold under "open" formulas. In the case of closed formula feeds, the ingredients are listed, but their respective proportions are not given on the feed tag; in open formulas, the amounts of the ingredients are listed. There is no one best ration that can be prepared to meet all existing conditions, and the ingredients in a mixed feed can be varied considerably to take care of economic conditions, if minimum allowances of certain essential nutrients are provided. Mixers must constantly be alert to variations in price of alternate ingredients that might be used if they are to compete with whole natural feeds and with other feed mixers. Mixed feeds must be sold on the basis of guaranteed minimum protein, fat, and nitrogen-free extract contents, and guaranteed maximum crude fiber and ash contents. Violations of these requirements are punishable within states where the feeds are sold, and federal laws are involved if feed enters interstate commerce.

Most large feed manufacturers use line mixers, while batch mixers are used in preparing small volumes. In line mixing the ingredients are added at controlled rates as the mix is augered along a line; when feed molasses is added its temperature is regulated to control consistency. Batch mixes are usually prepared by adding all ingredients to a specially constructed hopper and augering the mix until it is uniform. Minor additions or special ingredients are usually premixed with some feed before being added for the final mixing.

Mineral feed mixes are prepared and sold for various classes of livestock and may give an economic response if added to rations deficient in some essential element they carry. However, the minerals most likely to be lacking in livestock rations are sodium chloride and phosphorus and calcium compounds, and these can be cheaply supplied as common salt, steam bone meal, defluorinated rock phosphate (see *Fertilizers*), and ground limestone.

In recent years other elements such as cobalt, iron, copper, and iodine have been found lacking in certain localities (15). When a ration is deficient in any mineral element, it may prove not only to be a depressing factor in the response of the animal to feed, but may result in appearances of malnutrition or poor performance even though an abundance of feed is supplied and other nutritional requirements are satisfied. Often a purchaser of a mineral mixture buys many ingredients and even trace elements already present in abundant quantities in the rations he feeds. A feeder can easily learn from unbiased sources of possible deficiencies in rations or probable trace mineral deficiencies in crops grown in a specific area. Condiments or conditioners are widely prepared and sold for livestock feeding. These should be used only upon the advice of a veterinarian or trained nutritionist not interested in the sale of the product (2). Their addition to well-balanced rations that are fed in ample quantities is seldom indicated.

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**FELDSPARS.** See *Ceramics (whiteware)*, Vol. **3**, p. 547; *Silica and silicates*.

## FELT

Felt is a textile composition produced without the use of the customary spinning and weaving techniques but rather through the exercise of pressure and friction, which bring about the interlocking of fibrous materials such as woolens, furs, and artificial staples, causing their compaction into a tough mat. Heat and moisture assist the felting process. The early origin of felt, which may be legendary, is said to have issued from the practice that camel drivers had of packing the inside of their sandals with camel's hair. The pressure exerted during walking, aided by warmth and perspiration, matted this hair and produced a felt. Most textile fibers (vegetable, animal, and synthetic) possess this quality of matting to some extent, particularly when in hot water and within certain pH ranges. Yet, actually, wools, furs, and some hairs are the only fibers that produce a true felt (see *Fur*; *Wool*).

In the fur-garment industry felting is avoided, whereas in the hatting industry it is the most important factor of the entire process.

There are divided opinions concerning the phenomenon of felting. One is the barb theory, which seeks to explain felting by noting that the structure of fur when examined microscopically shows barbs or spurs or sheaths that cause the hair to be rougher when rubbed in the tip-to-root direction than in the reverse direction. According to this theory, under pressure and in hot water the treated fibers lock into each other, and the individual fur fibers shrink, thus producing a tough-textured final product. However, this cannot be the only factor at work for there are varieties of raw furs (for instance, cat fur) whose barbs are as sharp as arrowheads, although they do not possess the felting property.

The probable explanation of felting lies in a combination of many factors, among



which are: the amphoteric nature of the chemically treated fur substance; the mucilaginous oozing of the plastic cortical matter between the intermeshed scales or barbs; the effect of surface tension (noted by the fact that fur completely and continuously worked under boiling water will not make good felt); and, lastly, the fact that, as the pith and cortex of the individual fiber swells laterally, the fiber shortens in length and tightens the scales accordingly in such wise that intertwining and interlocking of the fibers become more certain. Furthermore, the carotting process purposely affects only the portion of the fiber away from the root, thus making the tip "softer" than the lower portion.

Certain so-called felts (frequently called velvet felt) are not felt in any sense of the word. Actually these cloths are made from wools having a high natural tendency to felt by spinning into yarn and weaving in such a way that a certain amount of felting will occur in the process. A true felt is a structure produced without spinning or weaving.

Felt may be considered in three groups: (1) wool felt, (2) felts products by impregnation, and (3) fur or hat felt.

**Wool Felt.** The classification of wool according to its felting quality depends upon its source. It requires no chemical treatment, as do fur fibers, to have the desired interlocking action. Woolen fibers are generally short to medium in length. They are first blended and then run through a series of manufacturing processes, called by terms peculiar to the trade. The order of the steps is: willying, blending, teasing, scribbling, carding, forming, hardening, milling, carbonizing, dyeing, and finishing. These processes vary as, indeed, does the machinery.

When the batts have been made, they may be superimposed on each other to produce a thick felt, or extended end to end and hardened from then on in such a way that the thickness is controlled and not the area, whereas in the subsequent milling process the area is affected considerably and the thickness is not changed. At this stage the felt is still weak and the fulling or strengthening processes are then used, the felt stock being continuously hammered until the proper dimensions are achieved and a material of considerable strength is made.

Depending upon their prospective uses, wool felts may be made of different weights, qualities, and toughness. Such felts can vary from 2 oz. per square yard to 30 lb. As in some of the padding used for insulation and polishing, felts can vary in thickness from  $\frac{1}{16}$  in. to 4 in. Manufactured felts are used for upholstery materials, carpeting, billiard tables, shoe felts, oddments of clothing such as shoulder pads, and all types of individual heat-insulating and silencing felts, piano and organ felts, and divers other forms.

**Impregnated Felts.** These felts are really not felts at all any more than paper batts might be termed felt. Such impregnated felts as are used in roofing, in housing and shipping sheathing, or for pads under carpets are made of coarse batts from vegetable-fiber waste that are impregnated and held together with an emulsion of bituminous material, plastics, or resins (see also *Bituminous roofing materials*).

**Fur or Hat Felt.** Hat felt is usually of animal origin. Coney, hare, and muskrat fur are the usual ingredients and nutria and beaver fur are used in the very expensive hats. Recently hatters have been including small amounts of synthetic fibers such as protein fibers made from casein, corn, soybeans, or peanuts. Generally speaking, the addition of even 10% of these fibers lessens the quality of the hat. While these fibers dye and are controlled almost as well as the customary animal fibers, they do not truly

felt but merely mat together under the influence of moist heat to produce something resembling a clotted plastic substance within the finished fur felt.

*Carrotting.* Felting is enormously facilitated by the process known as carrotting, which consists in heating the fur, on the pelt, with certain oxidizing agents in acid solution. The chemistry of the process is not fully understood, but cross linking between protein molecules is probably involved, and the significance of the acid probably lies in the fact that the isoelectric point of fur substance, where its degree of hydration is a minimum, is at about pH 4.8.

For over a century, felting for hat manufacture was accomplished with a solution of mercury in nitric acid, using secret formulas handed down from father to son. Fur thus treated turns yellow like a carrot (whence the name). This may be compared with the action of Millon's reagent (mercuric nitrate) as a test for certain proteins.

A grave objection to mercurial carrots is the poisonous character of mercury (*q.v.*). In some operations in the plant, the fur is subjected to relatively high temperatures and to air sifting, and the mercury vapor (or dust) constituted a health hazard. Hatters of the mercury-carrott age had poor eyesight, poor teeth, poor kidneys, poor hearts, indeed, poor everything. Mercury-carrotted fur may contain from 2 to 3% of mercury, and about one-third of this is released into the atmosphere during manufacture. Thus about  $1\frac{1}{2}\%$  is left in the finished hat (3 oz.), which will accordingly contain about 1 gram of mercury.

This mercury carrot in all its forms is now interdicted in the U.S. through a regulation of the U.S. Public Health Service. Yet, peculiarly enough, fur so carrotted in foreign countries, chiefly Belgium, France, and England, is permitted into the country for hat manufacture. This does not seem fair to U.S. fur cutters, who rely upon the use of various so-called nonmercurial carrots, most of which are patented. These nonmercurial carrots are usually made from about 20- to 25-vol. hydrogen peroxide catalyzed by nitric acid and other chemicals. The Frank H. Lee Co. of Danbury, Conn., was chiefly responsible for this great progress in the hatting industry; their peroxide carrot is the most widely used in the U.S. as well as in Europe. Compounds of chlorine (hypochlorite, chloric acid, perchlorates) are also used in certain patented combinations.

The carrotting solution of proper strength is applied by dipping a brush into the solution and then rubbing it into the fur. It is very important that the carrot be rubbed thoroughly into the fur and all excess solution be removed from the surface of the skins, since such an excess tends to damage the tips of the fur fibers. The skins are then piled on top of each other (fur to fur) in stacks of about 25-50 skins and allowed to remain in this state 15-30 minutes. This piling aids in getting the solution uniformly spread throughout the fur and at the same time offers a definite reaction period for the carrotting solution on the fur fibers. The furs are then spread on racks or conveying aprons and taken to the dryer.

It has been determined that the more quickly the skins are dried and the higher the temperature used, the faster the shrinkage of the fur and the better the quality of the felt. Prolonged drying with insufficient heat or ventilation is detrimental and produces inferior quality fur. Drying can be accomplished in two ways: (1) in a drying room where the temperature is kept around 120°F., which produces very satisfactory results but requires several hours for drying (generally perfect drying can be obtained overnight, and many manufacturers, usually small ones, use this method); (2) in conveyors (specially built dryers where the skins are continuously moving through the drying zone) at a temperature of from 165 to 200°F.

Skins are never dried fur to fur, but open, or fur up. After the skins have been carrotted, they must not be piled and left overnight, as was the procedure with mercury. After the skins are dried, the fur can be cut immediately or within any length of time desired. It is not necessary to age fur after it has been carrotted, as was done with mercury carrott. Hats can be made immediately after the fur is cut, or the fur can be stored for an indefinite period without deterioration.

*Felt Hat Manufacture.* After carrotting the fur is cut from the felt by a machine, and then blown (air-sifted) and blended in various combinations. Carrotting is seldom uniform—even coney furs from different geographic sources have different felting qualities—and usually many furs are blended together in an effort to get some degree of uniformity. About 10% of uncarrotted raw fur (in the U.S., muskrat, which is usually recovered from scraps by an ingenious hydrolyzing process; in Europe, hare or coney) is added to the blend so as to produce a lustrous surface or veneer upon the hat. Sometimes for pastel shades the fur is colored at this point—sometimes not. (Small hatting concerns purchase cut fur, or blown fur, as it is called, and this material has been so frequently adulterated that it has been most unsafe to procure it except after proof, by experiment, of its hat-making possibilities.)

A quantity of blended fur mixture is then blown on a large, revolving, perforated cone about two or three times the height of the finally sized hat, the fur surface meanwhile being kept moist with warm water or steam. The cone size chosen depends largely upon the mixture. Thus a poorly felting fur is given a smaller cone, the better felting fur a larger cone.

This cone with its veneer of fur is then dipped for a time into moderately hot water, lifted out, and inverted, and the flimsy fur body is slipped off. This thin form is now worked through various operations (hand or mechanical or combinations of both) until it felts and shrinks to a much-reduced cone shape; sometimes the hat is colored at this stage. Next a shellac solution, aqueous or alcoholic and white or amber, is forced into the lower rim of the cone, so as to provide the desired rigidity and plasticity to the brim of the finished hat. Inferior hats are frequently shellac- or gum-stiffened in the crown as well as in the brim.

This cone shape is then plunged in boiling water, rounded out at the tip, and pulled out or bent at the band, in order to differentiate the crown and brim. This rough body is stretched over a block to its desired shape. Finishing and trimming are next in order. All together, some fifty-six odd operations are required to build a good, soft, felt hat.

The demand for pastel colors in the fur-felt hat trade and the shortage of white rabbits has increased the demand for processes whereby the common gray rabbit fur may be changed to a white or near white. This has been done successfully in the fur-garment trade, but not so successfully for hat fur because it weakens the strength of the felt. However, for pastel purposes it is possible to modify background colors with alkaline peroxides in such a way as to improve them over the gray shades.

IVOR GRIFFITH

**FENCHENES**,  $C_{10}H_{16}$ . See *Terpenes and terpenoids*.

**FENCHONE**,  $C_{10}H_{16}O$ . See Vol. 1, p. 355; *Terpenes and terpenoids*.

**FENCHYL ALCOHOL**, **2-FENCHANOL**,  $C_{10}H_{17}OH$ . See *Terpenes and terpenoids*.

**FENNEL OIL.** See *Oils, essential*.

**FERBERITE**,  $\text{FeWO}_4$ . See *Tungsten*.

**FERGUSONITE**,  $(\text{Y,Er,Ce,Fe})(\text{Cb,Ta,Ti})\text{O}_4$ . See *Columbium*, Vol. 4, p. 316.

## FERMENTATION

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See also *Enzymes*; *Microorganisms*.

### Definitions

The word fermentation originates from Latin and in its narrower sense it has been used to designate the transformation of grape juice into wine. The Latin word *fervere* originally meant "boiling" and was used as a metaphor to describe the effervescent appearance of the fermenting grape juice. In several modern languages, the same word is applied to describe the boiling of heated water as well as the gas formation in actively fermenting sugar solutions. The first biochemical explanation for the process in which sugar in aqueous solution is decomposed into alcohol and carbon dioxide, owing to the action of living yeast cells, was given by the French chemist Louis Pasteur. He recognized that, while decomposing the sugar in the absence of air, yeast cells live and propagate in the fermenting liquid, and he called the process of alcoholic fermentation "life without oxygen." He explained that, through the cleavage of the sugar molecule in the absence of air, energy is made available for the yeast cells just as energy is produced in the respiring tissues of animals and plants for their metabolic needs when organic compounds are oxidized in the presence of air.

Pasteur's explanation was modified by Büchner, who showed that fermentation could be carried out in aqueous sugar solution by the press juice obtained from dead yeast cells. The filtered juice of yeast cells that had been ground with sand was then found to contain a substance efficacious in cleaving sugars, and this active substance or mixture of catalyst was named *ferment*, *enzyme*, or *zymase*. The theory of the action of microbial enzymes in fermentation that developed following this discovery did not change in respect to the fact that in the fermentation process energy is liberated that can be utilized by the yeast cell in the absence of air.

By extending Pasteur's biochemical interpretation of alcoholic fermentation to other processes, *fermentation* today denotes the anaerobic dissimilation of organic compounds due to the action of microorganisms or other cells and extracts prepared from them. However, in many technical papers, and even more so in everyday laboratory and plant usage, the term fermentation is favored as including microbial action controlled by man. In this wider sense, fermentation not only denotes anaerobic dissimilation processes like the formation of alcohol, butanol-acetone, lactic acid, etc.,

but also the industrial production of vinegar, citric acid, enzymes, penicillin and other antibiotics, and riboflavin and other vitamins, since they all result from microbial processes and are therefore termed "fermentation products." Similarly, "fermenter" is the common term not only for the reaction vessels in which fermentation is conducted with the exclusion of air but also for tanks in which aerobic microbial oxidations are conducted or for propagating tanks in which yeast and other organisms are propagated in the presence of air.

The term *microorganism* denotes plants, generally microscopic in size, that belong to the subdivision Fungi of the Thallophyta (see *Microorganisms*; *Yeasts*).

The kingdom of plants is divided into four groups: (1) seed-bearing plants, *Spermatophyta*; (2) ferns, club mosses, and horsetails, *Pteridophyta*; (3) mosses and liverworts, *Bryophyta*; and (4) plants growing in thallus form (having no true roots, leaves, trunks, or vessels), *Thallophyta*. The thallophytes fall into three subgroups: algae, lichens, and fungi. The several hundred thousand species of fungi form three divisions: slime molds, *Myxomycetes*; bacteria, *Schizomycetes*, and true fungi, *Eumycetes*. The microorganisms applied in industrial processes belong to the last two divisions: the bacteria and the true fungi (which includes molds and yeasts, among other forms).

Individual species of microorganisms are distinguishable one from the other by morphologic characteristics and by biochemical behavior. The microscopic and macroscopic appearance of bacteria, yeasts, and molds, and the products of their dissimilation are well studied and are used in their identification. The formal classification of microorganisms follows several lines and is still awaiting unification. But among the thousands of species of the naturally occurring microorganisms capable of effecting one or another type of fermentation or related activity, only several dozen, selected because of their ability to direct their activity along one desired pathway, are utilized in controlled processes. Hundreds of species of yeasts, bacteria, and molds are known to produce alcohol, for example, yet hardly more than two or three species of yeast are industrially applied in the production of alcohol or alcoholic beverages; their speed in fermentation, tolerance to high concentrations of sugar and alcohol, and high yield of alcohol favor their use over all others. Some organisms even find more than one application industrially. Yeasts, for instance, produce alcohol and glycerol from sugars, raise dough in breadmaking, and are a source of proteins, vitamins, and enzymes. Specific examples are: *Saccharomyces cerevisiae*, the common yeast, which is considered as "domesticated" among microorganisms as are wheat, corn, and potatoes among plants, and cats, dogs, cows, and horses among animals; *Aspergillus niger*, a mold employed in producing citric acid, gluconic acid, oxalic acid, and amylase, and in vitamin synthesis; and *Lactobacillus delbrueckii*, which is used in lactic acid, sour pickle, and sour mash production.

Table I lists the most popular microorganisms in current industrial fermentations. It is worth noting that the number increases constantly with the development of new processes.

The expression *microbial metabolism* includes all enzymic processes involved in growth, development, and maintenance of the cell. These are generally classified as *dissimilation*, *assimilation*, and *biosynthesis*. (The terms "catabolism" for dissimilation and "anabolism" for assimilation and biosynthesis are also occasionally used.)

### The Fermentation Process

In common application, the term fermentation is used synonymously with all the terms denoting various microbial actions. In microbiology, however, fermentation

refers only to a well-specified type of microbial action. In the cytology of higher organisms, fermentation denotes biochemical processes which show characteristics similar to microbial fermentations. For this reason, the fermentation process must be shown in line with the other microbial actions specifying its relative position to them and to the nearest biochemical action of tissue cells. In borderline cases, as will be seen, the term fermentation and the term respiration still overlap in meaning as used by the microbiologists and by the cytologists of higher organisms.

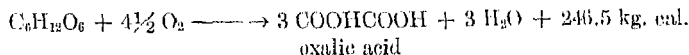
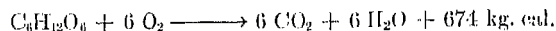
All microbial actions, for practical purposes, may be grouped as growth, assimilation, biosynthesis, and dissimilation. *Growth*, which refers to the microindividual as well as to a whole group of organisms living together as a colony or a culture, includes the increase of the cell size and the reproduction of the cells and individuals directly by splitting, budding, or through formation of special bodies such as spores and conidia. *Assimilation* is the activity by which the various components of the substrate are transformed into the cell substance, thus providing material necessary for growth and life activities. *Biosynthesis* is the formation of complex compounds within the cells in quantities greater than necessary for the maintenance of normal life activities. Biosynthesized compounds, which usually are essential biochemically active substances (enzymes, vitamins, antibiotics, toxins, etc.) may remain within the cell walls but are quite frequently eliminated from the cell into the substrate. Biosynthesis is usually nonspecific to a species but specific to a strain. Both assimilation and biosynthesis collectively are called anabolism and are energy-consuming processes for which the energy is provided by dissimilation or catabolism. In *dissimilation*, compounds of the substrate which the organism is capable of utilizing as sources of energy, or compounds within the cell like glycogen and adenosine triphosphate (ATP), which the organism prepares for energy reserve, are changed into new products having less energy than the compound from which they are formed, so that energy is liberated. Dissimilation occurs within the cell, and the products are expelled into the surrounding medium. Subject to dissimilation are most naturally occurring organic compounds, a few inorganic compounds, and some elements. Examples are carbohydrates, glycosides, mono- and polybasic alcohols, aldehydes, mono- and polybasic acids, keto and hydroxy acids, hydrocarbons, amino acids, and amines; some iron, manganese, and arsenic salts; elementary carbon, sulfur, etc.

Dissimilation processes are oxidative in nature and may be accomplished by: (1) the addition of oxygen, (2) the removal of hydrogen, or (3) the loss of an electron. Most frequent is the removal of hydrogen (the dehydrogenation process) from the mother substance, the hydrogen donor. The hydrogen is transferred by a hydrogen carrier or a series of carriers (like enzymes and respiratory pigments) to a reducible substance, the hydrogen acceptor. Atmospheric oxygen, one or more of the intermediate compounds formed during the dissimilation process, or another reducible compound present in the substrate may act as hydrogen acceptor.

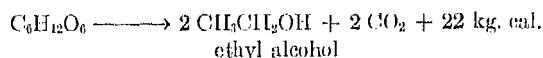
If atmospheric oxygen, entering into the reaction, acts as hydrogen acceptor, the dissimilation process is aerobic (or oxibiotic). When it is accomplished without participation of atmospheric oxygen, the dissimilation is true fermentation (or anaerobic dissimilation). The substrate, for instance glucose, may be oxidized completely by aerobic dissimilation to yield water and carbon dioxide, but it may be oxidized to varying degrees to yield incomplete oxidation products such as gluconic acid, saccharic acid, citric acid, and oxalic acid. The fermentation process usually fragments the mother compounds. When fermented, 1 molecule of glucose may yield 2 molecules of

ethyl alcohol and 2 molecules of carbon dioxide, or 2 molecules of lactic acid, etc. The energy liberated by aerobic oxidations is far greater than that liberated by fermentation processes:

*Aerobic oxidations:*



*Fermentations:*



In both cases only a fraction of the liberated energy is utilized for assimilation, biosynthesis, and maintenance of normal life, while the major part appears in the form of heat.

The oxidation of glucose in the cells of higher organisms is performed in two phases. In the first phase, lactic acid is formed by an energy-yielding anaerobic process (glycolysis), and in the second phase, with the participation of oxygen, a portion of the lactic acid is oxidized through a series of steps to water and carbon dioxide, while the rest of the lactic acid is converted into glucose. Because of its similarity to microbial fermentation processes, the first anaerobic phase is called **fermentation**, and the second phase, because it is tied up with the inhalation of air and exhalation of the products of combustion, is termed **respiration**.

Microbiology adapted the term respiration to denote collectively both aerobic and anaerobic energy-yielding dissimilations. Since some organisms obtain energy by oxidation without air exclusively, it seemed logical to consider such processes identical in function to the aerobic oxidation processes occurring in other organisms. As the result of borrowing terms from each other, respiration in microbiology has a broader meaning than in cytology. All microbial enzymes taking part in energy-producing dissimilations are collectively called respiratory enzymes.

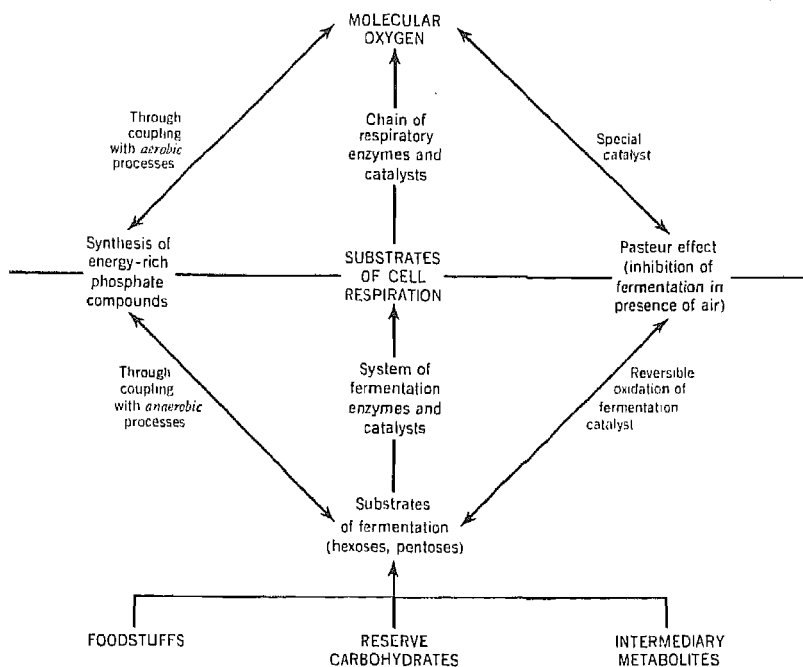
With regard to the method of dissimilation (respiration), microorganisms are of three types: (1) obligatory anaerobes live and dissimilate only in absence of air and respire by fermentation only; (2) obligatory aerobes live and dissimilate only in the presence of air by aerobic oxidation only; and (3) the facultatives, breaking down into several subgroups according to their sensitivity to oxygen, may live and respire in the absence or in the presence of air.

In several respects, microbial cells exhibit similar behavior to the cells of higher organisms; fermentation activity of the anaerobes and the facultatives resembles the glycolysis of tissue cells, and the aerobic dissimilation of the aerobes and facultatives resembles the tissue respiration.

Pasteur observed that the fermentation activity of yeast is suppressed when oxygen is made available, and aerobic oxidation will take its place. The influence of oxygen on the means of dissimilation is called the "Pasteur phenomenon," "Pasteur effect," or "Pasteur reaction," and it was found valid for some microorganisms other than yeasts and for respiring cells of higher organisms. The best definition of the Pasteur effect according to Dixon and Stern is "the action of oxygen in diminishing carbohydrate destruction and suppressing or decreasing the accumulation of the prod-

ucts of anaerobic metabolism." The Pasteur reaction is believed by some workers to be governed by a hypothetical enzyme, the Pasteur enzyme.

Scheme 1. Energy-Yielding Processes in Living Cells.



Scheme 1 illustrates the possible mechanism of glucose dissimilation by cells, including the relationship of the Pasteur reaction. While several facultative microorganisms (species of *Rhizopus*, *Mucor*, *Dematium*, *Sachsia*, *Saccharomyces*) do exhibit the Pasteur phenomenon, many others do not. Homofermentative lactobacilli ferment glucose into lactic acid under both aerobic and anaerobic conditions; *Aerobacter aerogenes* and *Bacillus polymyxa* ferment glucose into 2,3-butanediol, ethyl alcohol, carbon dioxide, and hydrogen under aerobic and anaerobic conditions. In fact, fermentation by *A. aerogenes* is greatly accelerated by strong aeration. Another difference is that while the respiring tissue cells in the presence of air completely oxidize the products of muscle fermentation, the aerobic respiration of many microorganisms is an incomplete oxidation and the products contain considerable potential energy. Typically characteristic of microbial respirations is the fact that the products may accumulate in considerable amounts: concentrations of 15–20% alcohol, 2% lactic acid, 10% citric acid, or 10% acetic acid produced by the microorganisms are possible in the substrate, while in tissue metabolism the fermentation intermediates and the oxidation products are kept at very low concentrations.

Both fermentation and respiration are complex processes requiring the participation of numerous enzymic and nonenzymic catalysts (see Vol. 5, p. 736) for their completion. In fermentation, a number of intermolecular oxidation-reduction reactions occur; in respiration, the hydrogen, available from certain substrates, is transported with the aid of specific enzymes (dehydrogenases) to a point at which it is "burned"



by iron-containing catalysts with the help of oxygen. Although the fermentation and the respiration of simple carbohydrates are the chief sources of cellular energy, the form in which the energy is made available does not lend itself to all types of vital functions. For this reason, the fermentation and respiration energy is largely utilized by the cell for the synthesis of energy-rich phosphate compounds (for example, adenosine triphosphate). Large amounts of "quick" energy are obtained from such phosphate compounds by enzymic fission. For this reason, substances of the type of adenosine triphosphate or creatine phosphate may be considered the "storage batteries" of the cell which are "charged" by the energy produced by fermentation and respiration.

Another basic difference between higher organisms and microorganisms is that tissue cells dissimilate to the extent of their need, while cells of microorganisms liberate energy by dissimilation far above their requirement. Their respiration activity is governed by external factors, such as the pH, temperature, oxygen tension, concentration of the substrate, and products in the medium, rather than internal necessity. In most instances, the bulk of the substrate is fermented or oxidized after the organism has completed or nearly completed its maximum growth. Considering that the dissimilation products are useless or even inhibitive to life for many organisms which may easily utilize the mother compound, and considering that its own dissimilation product by many organisms under certain conditions may be assimilated or further dissimilated, we may assume that microbial respiration, besides its primary purpose, energy liberation, is a means of self-protection and food preservation.

### Microbial Enzymes and Coenzymes

Enzymes are proteins or conjugated proteins produced by living cells and possessing the power of catalyzing specific reactions without being used up in the process or becoming a part of the products formed. Each enzyme is highly specific with respect to the substance or substances upon which it acts and to the reaction which it catalyzes. The ability to catalyze a reaction in both directions has been demonstrated for many enzymes, and it is believed that the same is true, at least theoretically, for all enzymes. It is also known that the same reaction may be catalyzed by a number of related but not identical enzymes formed by different organisms. Contrary to former belief, enzymes do take part in the catalyzed reactions, forming intermediate compounds with the substrate, and also may initiate reactions.

All enzymes have been found to form colloidal solutions and to have high molecular weights, usually from 20,000–100,000 but occasionally much higher (urease 483,000). They usually differ with regard to their optimum temperature, optimum pH, optimum enzyme and substrate concentration, equilibrium constant, etc. Enzymes prepared from the cells of microorganisms have the same general properties as those prepared from the tissues of higher plants and animals. Within its body, which often weighs less than a tenth of a billionth of a gram, a unicellular organism contains scores of various enzymes, for the major part of its vital activity is due to enzymic reactions.

*Exoenzymes* (see also p. 325) are the enzymes secreted by the cells into the medium, where they catalyze (mostly hydrolytic) reactions independent of the cell. *Endoenzymes*, like most enzymes active in respiration, assimilation, and biosynthesis, remain and act within the cell wall. The border between the two groups, exoenzymes and endoenzymes, is not sharp.

The article *Enzymes and enzymology* (Vol. 5, pp. 735–62) discusses in greater detail

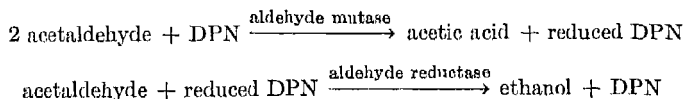
the nature, function, classification, preparation, and uses of enzymes in general. Some specific enzymes are also described, and the relation of enzymes to coenzymes and proenzymes (zymogens) is clarified. Because coenzymes and a countless number of specific enzymes are involved in the fermentation processes, this article will list the most familiar.

### COENZYMES

Coenzymes generally contain growth factors, or vitamins of the B group, and one or more phosphate radicals. The best-known microbial coenzymes may be grouped conveniently as follows: pyridine coenzymes; thiamine coenzymes (cocarboxylase); alloxazine coenzymes; adenylic acid coenzymes; and miscellaneous coenzymes.

**Pyridine coenzymes**, components of the zymase system, comprise two important members: coenzyme I (or cozymase) and coenzyme II. Their structural formulas differ only in that cozymase (see Vol. 5, p. 741) contains two, and coenzyme II contains three, phosphoric acid groups. On hydrolysis, besides the phosphoric acids, they yield one molecule of nicotinic acid amide (nicotinamide); this is the active group capable of being reduced and reoxidized and thus able to take part in hydrogen transfer as an intermediate hydrogen acceptor, one molecule of adenine (6-aminopurine), and two molecules of pentose. Chemically, they are diphosphopyridine nucleotide (DPN) and triphosphopyridine nucleotide (TPN). In spite of the fact that DPN can be converted into TPN by chemicals, enzymes, and microorganisms, the two coenzymes may substitute for each other only infrequently. Generally, the specific enzymes specifically require either DPN or TPN. The two nucleotides are easily reduced by sodium hydrosulfite and again reoxidized by methylene blue or by the yellow enzymes in the presence of air. In addition to transferring hydrogen, DPN is capable of transferring phosphate. Phosphate transfer is inhibited by sodium ions and aided by manganese ions and ammonium and potassium salts. These facts have found application in alcoholic fermentation.

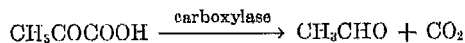
The best-known enzymes of which coenzyme I is the prosthetic group are: alcohol dehydrogenase (or aldehyde reductase),  $\beta$ -hydroxybutyric dehydrogenase, lactic dehydrogenase, malic dehydrogenase, glucose dehydrogenase, triosephosphate dehydrogenase, and aldehyde mutase. Two of these oxidation-reduction reactions may be represented as follows:



Coenzyme II is the prosthetic group of the following enzymes: glutamic acid dehydrogenase (in yeast; some higher plants contain coenzyme I-linked glutamic acid dehydrogenase), hexose monophosphate dehydrogenase, and isocitric acid dehydrogenase.

Pyridine nucleotides are considered essential for all organisms. Some organisms like yeasts are able to synthesize all their coenzymes from carbohydrates, ammonium salts, and phosphates, while others may require in the culture medium some or all of the simple components (nicotinamide, phosphates, pentose, adenylic acid), and still others depend upon a supply of the complete coenzymes.

**Cocarboxylase** is diphosphothiamine, the pyrophosphoric acid ester of vitamin B<sub>1</sub> (see *Thiamine*), and is the prosthetic group of the enzyme *carboxylase*, which catalyzes decarboxylation reactions (the splitting of carbon dioxide from  $\alpha$ -keto acids with the formation of the corresponding lower aldehyde). Carbon dioxide, the characteristic gaseous fermentation product, is formed by carboxylase. A typical reaction catalyzed by carboxylase is the formation of acetaldehyde from pyruvic acid:

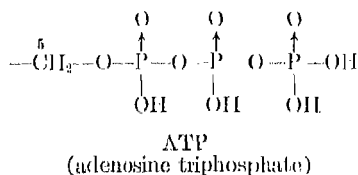
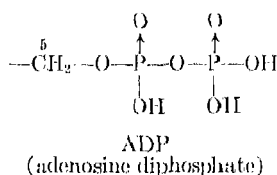
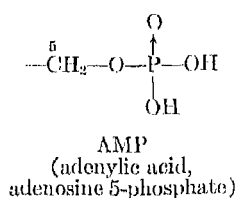
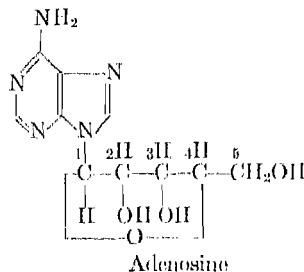
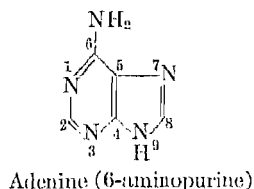


**Alloxazine (flavin) coenzymes** are phosphoric acid esters of riboflavin (vitamin B<sub>2</sub>, or 6,7-dimethyl-9-(1-D-ribityl) isoalloxazine). The prosthetic group of Warburg's old "yellow enzyme" (yellow ferment), which oxidizes Robison ester (glucose 6-phosphate), is riboflavin phosphate (see Vol. 5, p. 741); the prosthetic group of the Warburg-Christian enzyme, D-amino acid oxidase, is an adenine flavin dinucleotide. In the latter, the two phosphate radicals, one riboflavin phosphate and

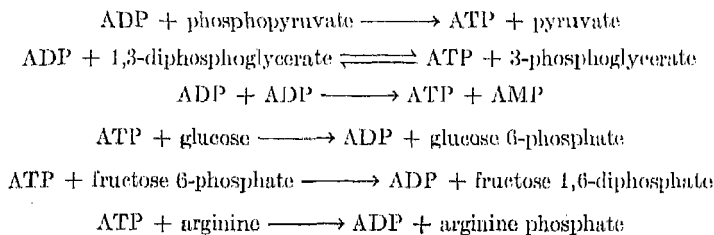
the other adenylic acid, are linked by an oxygen bridge. Yellow enzymes as a rule catalyze oxidation-reduction reactions. The green fluorescence and yellow color of the coenzyme solutions are due to the riboflavin part. They disappear on reduction and reappear when shaken with air.

Alloxazine coenzymes take part in transferring hydrogen from the substrate to molecular oxygen. As part of specific enzymes, they catalyze the oxidation of Robison ester,  $\alpha$ -amino acids, xanthines, reduced DPN, reduced TPN, and glucose.

The alloxazine coenzymes (also called flavoproteins) that oxidize reduced coenzyme I and coenzyme II are called diaphorase I and diaphorase II, respectively. The enzyme cytochrome reductase, which reduces cytochrome c, is also a flavoprotein and possibly is identical with diaphorase II. The enzymes L-lysine decarboxylase and acetoacetic acid decarboxylase are probably also flavin enzymes. Flavoproteins and their coenzymes are widely distributed in nature and take active part in the metabolism of most aerobic microorganisms.



**Adenylic acid coenzymes**, that is, adenosine 5-monophosphate (muscle adenylic acid, also known as AMP), adenosine diphosphate (ADP), and adenosine triphosphate (ATP), differ only in the number of phosphate radicals. By accepting or giving up a phosphate residue, one may be transformed into another. They take part in enzymic reactions that split or transfer energy-rich phosphate bonds. The following reactions illustrate some of their activities (see also Scheme 2, p. 354):



The energy-rich phosphate bond of ATP is split by the enzyme adenosine triphosphatase (apyrase), or it is utilized in the phosphorylation of substrates and intermediates in the various metabolic processes. The terminal phosphate of the ATP is more reactive than that of ADP.

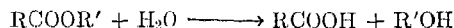
**Miscellaneous Coenzymes.** Other heat-stable, dialyzable parts of enzymes (that is, the coenzymes) than those listed above are also known to be present in microorganisms. Some of them are coenzyme R, glyoxalase coenzyme, and lysine decarboxylase coenzyme. *Coenzyme R*, essential to the nutrition and respiration of the root bacteria *Rhizobium*, is possibly identical with or related to biotin, a member of the vitamin B group. *Glyoxalase coenzyme* is glutathione or contains glutathione, a tripeptide ( $\gamma$ -glutamylcysteinylglycine). It is necessary for the action of the enzyme glyoxalase, which converts methylglyoxal (pyruvaldehyde) into lactic acid. However, it combines with the substrate rather than with the enzyme, and its designation as a coenzyme is, therefore, questionable.

*Lysine decarboxylase coenzyme*, believed to be a flavin coenzyme different from those already known, catalyzes the decarboxylation of L-lysine to cadaverine.

### HYDROLYZING ENZYMES

Microbial hydrolases are often called the digestive enzymes of the microorganisms, and the process of hydrolysis is called digestion. Most hydrolytic enzymes are extracellular (exoenzymes) and are excreted into the surrounding medium from the microbial cell. Before their assimilation, the polysaccharides, proteins, peptones, peptides, alcohol esters, phosphoric acid esters, glycerides, and other compounds in the process of hydrolysis, while accepting water, are split into simpler components. The hydrolases will be described here in three major groups: esterases acting on esters; carbohydrases acting on compound carbohydrates; and proteases acting on proteins and related nitrogen compounds.

**Esterases**, whose action is symbolized by:

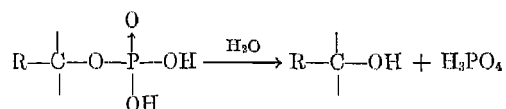


are composed of four groups: (1) lipases, (2) lower esterases, (3) phosphatases, and (4) sulfatases:

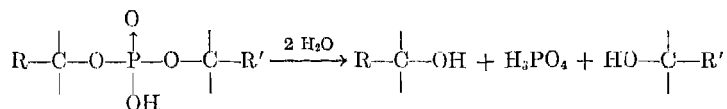
(1) *Lipases*, which hydrolyze neutral fats into glycerol and fatty acids, are both intracellular and extracellular enzymes and widely distributed in yeasts, molds, and bacteria (also in higher plants and in animals). In fats, 0.3% moisture permits microbial growth and the action of the lipases produced. Some bacterial lipases exhibit considerable resistance to heat.

(2) *Lower esterases* hydrolyze simple esters of lower fatty acids, like ethyl butyrate, into ethanol and butyric acid.

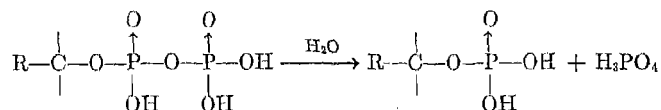
(3) *Phosphatases* catalyze the hydrolysis of phosphate radicals connected by ester linkage to organic compounds. The numerous phosphatases are grouped as phosphomonoesterases, phosphodiesterases, pyrophosphatases, lecithinases, and nucleotidases. (a) *Phosphomonoesterases* catalyze the reaction:



Common monoesterases are phytase, glycerophosphatase, and hexosephosphatase, which catalyze the hydrolysis of phytin, glycerophosphate, and hexose phosphates, respectively. (b) *Phosphodiesterases* catalyze the reaction:



(c) *Pyrophosphatases* catalyze the reaction:



(d) *Lecithinases* catalyze the hydrolysis of lecithin to glycerol, fatty acids, choline, and phosphoric acid and are present in a number of organisms. (e) *Nucleotidases* hydrolyze nucleotides into nucleosides and phosphoric acid.

(4) *Sulfatases* catalyze the hydrolysis of sulfuric acid esters, for instance, the hydrolysis of potassium phenyl sulfate into phenol and potassium sulfate. They are present in *Aspergillus oryzae* and other organisms.

Esterases are widely distributed in plant and animal tissues, are common in microorganisms, and play a role in both digestion and assimilation. Various esterases occurring in *Achromobacter*

*punctatum*, *Pseudomonas aeruginosa*, *Oidium lactis*, *Aspergillus niger*, *Penicillium glaucum*, *Bacillus subtilis*, *Protus vulgaris*, *Clostridium acetobutylicum*, *Aspergillus oryzae*, *Rhizopus japonicus*, *Saccharomyces cerevisiae*, and other organisms have been studied.

**Carbohydrases** catalyze the hydrolysis of higher carbohydrates into simple sugars, and they are widely distributed among microorganisms. The presence or absence of specific carbohydrases in microorganisms is often used for species identification. Carbohydrases are divided into: (1) polysaccharidases, (2) trisaccharidases, (3) disaccharidases, (4) glycosidases, and (5) glucoproteinases, according to the substrate upon which they act.

(1) **Polysaccharidases:** (a) *Cellulases* and *hemicellulases*, present in *Polyporus vaporarius*, *Merulius domesticus*, *Aspergillus oryzae*, and other organisms, hydrolyze cellulose and hemicellulose, respectively. (b) The *amylases* or *diastases* (present in many microorganisms, in germinating seeds, and in digesting juices of animals), one of the most important enzyme systems utilized in fermentation and related processes, catalyze the formation of maltose from starch. Each individual amylase has a different function:  $\alpha$ -*Amylase*, often called the "dextrinizing" enzyme, liquefies starch by dissolving the amylopectin of the starch kernels; it hydrolyzes starch rapidly to the achromic point but is slow in the production of maltose; the principal product is  $\alpha$ -maltose.  $\beta$ -*Amylase*, often called the "saccharifying" enzyme, will produce maltose rapidly but will approach the achromic point slowly. *Amylophosphatase* liquefies starch without production of maltose. *Limit dextrinase* hydrolyzes the limit dextrins to maltose. The proportion of the various amylase components, their optimum temperatures, and the optimum pH of the amylases originating from various sources have been closely studied. There is a marked difference among those originating from malt, molds, and bacteria. *Aspergillus niger*, *A. oryzae*, and several *Mucor* and *Rhizopus* species are rich sources of mold amylase. Most yeasts do not contain amylase, while some species of *Schizosaccharomyces* hydrolyze starch. *Bacillus subtilis*, *B. macerans*, *Clostridium butyricum*, *B. polymyxa*, and other bacteria produce bacterial amylase. (c) *Pectinase* hydrolyzes pectic acid into sugars and galacturonic acid. It is produced by various species of *Rhizopus*, *Micrococcus*, *Lactobacillus*, *Aerobacillus*, and other genera. (d) *Inulase* (*inulinase*) catalyzes the formation of fructose from inulin, the polysaccharide stored in the tubers of the Jerusalem artichoke, and is industrially applied in alcohol production. Inulase is produced by *Aspergillus niger*, *A. oryzae*, and *Penicillium* and *Citromyces* species, but not by *Mucor* or *Rhizopus* species. (e) *Glycogenase*, present in animal tissues and many microorganisms (primarily yeast and molds), produces glucose from glycogen. Glycogen is often accumulated as reserve food in well-nourished yeast cells and used up when the medium becomes deficient in carbohydrates. Recent work indicates that glycogen is primarily broken down by phosphorolysis rather than hydrolysis.

(2) **Trisaccharidases:** (a) *Raffinase*, known to be produced by *Aspergillus niger*, *Penicillium camemberti*, and bottom brewers' yeast (*q.v.*), hydrolyzes raffinose into fructose and melibiose. (b) *Gentianase* and *melezinase*, which hydrolyze the corresponding trisaccharides, are present in some bacteria. Gentianose is hydrolyzed into fructose and gentiobiose, and melezitose into glucose and sucrose.

(3) **Disaccharidases:** (a) *Invertase* (*sucrase* or *saccharase*), present in most yeasts and in many other microorganisms, hydrolyzes sucrose into glucose and fructose. (Hydrolyzed sucrose is often called invert sugar.) (b) *Maltase*, the most widely distributed microbial enzyme, produces two molecules of glucose from one molecule of maltose. (c) *Lactase*, present in several yeasts and in many molds and bacteria (*Saccharomyces fragilis*, *Oidium lactis*, *Escherichia coli*, *Lactobacillus bulgaricus*, *L. delbrueckii*), converts lactose (milk sugar) into glucose and galactose. (d) *Melibiose* converts melibiose into glucose and galactose. (e) *Cellobiase* converts cellobiose into glucose. (f) *Gentiobiase* converts gentiobiose into glucose.

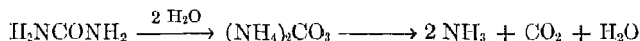
(4) **Glycosidases** hydrolyze glycosides into a sugar or sugars and other products. Disaccharides may be considered glycosides—sucrose is an  $\alpha$ -glucosyl  $\beta$ -fructoside, maltose an  $\alpha$ -glucosylglucose, and lactose a  $\beta$ -galactosylglucose. The specific enzymes will hydrolyze the specific  $\alpha$ - or  $\beta$ -linkage of a disaccharide or a glycoside. (a) *Arbutinase* hydrolyzes arbutin to glucose and hydroquinone. It is present in many molds, especially *Aspergillus* and *Penicillium* species. (b) *Amygdalase*, produced by yeasts and many molds (such as *Aspergillus niger*, *A. glaucus*, *P. glaucum*), splits amygdalin into benzaldehyde, hydrogen cyanide, and gentiobiose. (c) *Tannase* splits tannins into tannic acid and glucose. (d) *Coniferase* splits coniferin into coniferyl alcohol and glucose, and *salicinase* splits salicin into glucose and salicylic alcohol; both are present in intestinal bacteria.

(5) *Mucinase*, a glucoproteinase, hydrolyzes mucins into glucose and amino sugars and is present in *Clostridium perfringens*, *Streptococcus bovis*, and *S. hemolyticus* but is absent in *Escherichia coli*, *Bacillus subtilis*, and many other microorganisms.

**Enzymes Acting on Proteins and Other Nitrogen Compounds:**

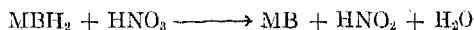
(1) *Coagulating enzymes*: (a) *Thrombin*, a blood-coagulating enzyme, is present in several bacteria. (b) *Rennin*, the milk-coagulating enzyme, has been demonstrated in yeasts and several bacteria; *Serratia marcescens* coagulates milk faster than rennin extracted from the calf stomach. (c) *Vitellase*, produced by *Bacterium anthracoides* and others, coagulates egg yolk.

(2) *Hydrolyzing enzymes*: (a) *Proteinases* readily catalyze the hydrolysis of natural proteins, but their activity (if any) on simple proteins is slow. Proteinases break the peptide linkage ( $-\text{CO}-\text{NH}-$ ) in the middle of long peptide chains. The optimum pH of most bacterial proteinases is 7.0–8.0 (but for pepsin 2.0–4.0, for papain 5.0, for trypsin 8.0–9.0). Usually present as exoenzymes in filtered media, a proteinase produced by yeasts hydrolyzes gelatin, casein, and so on and exhibits greatest activity at pH 1.8. Many molds and bacteria manufacture proteinases of differing characteristics. (b) *Peptidases (ereptases)* attack the terminal linkage of simpler proteins and are inactive on native proteins and on the final hydrolytic products—the amino acids. According to the linkage for which each is specific, they are grouped as carboxypeptidases, aminopolypeptidases, and dipeptidases. *Carboxypeptidase* attacks the peptide linkage only if a free carboxyl group is available on the side chain; it has been found in yeast and bacteria. *Aminopolypeptidase* requires for its action a free amino group or a basic nitrogen carrying at least one hydrogen atom on the end of the peptide chain; aminopolypeptidase has been isolated from yeasts and a great number of bacteria. *Dipeptidase* acts on dipeptides, requiring a free carboxyl and a free amino group; it is present in *Escherichia coli* and *Bacillus megatherium*. (c) *Nucleases* hydrolyze nucleic acids of the pentose and desoxypentose type with the formation of nucleotides. *Bacillus subtilis*, *B. vulgatus*, and *B. megatherium* are known to possess nucleases. Enzymes hydrolyzing nucleotides are often classified in this group. (d) *Arginase*, which hydrolyzes arginine to urea and ornithine, has a pH optimum of 9.0. Magnesium and cadmium will activate, and calcium and barium inhibit, its action. (e) *Urease* hydrolyzes urea into ammonium carbonate or ammonia and carbon dioxide:



This widely distributed enzyme is present in *Bacillus pasteurii*, *Sarcina ureae*, *Torula rubra*, *Schizosaccharomyces sautawensis*, *Aspergillus niger*, *Penicillium glaucum*, and others. (f) *Hippuricase* (or *histozyme*) hydrolyzes hippuric acid into benzoic acid and glycine; it also hydrolyzes some other homologs. Hippuric acid, which is produced by intermediary metabolism and eliminated from the animal body in the urine, is hydrolyzed by bacteria. (g) *Purinedesamidases* deaminate amino derivatives of purines. *Guanase* transforms guanine into xanthine and ammonia, and *adenase* deaminates adenine into hypoxanthine and ammonia. (Guanine and adenine are constituents of nucleotides, thus of nucleic acid.) These enzymes are produced by *Clostridium acidivirici* and by yeasts.

(3) *Miscellaneous enzymes* (not necessarily hydrolytic in nature): (a) *Creatinase*, present in soil bacteria, will decompose creatine into urea and other products. (b) *Nitratase* (or *nitrate reductase*), present in *Escherichia coli* and other organisms, reduces nitrates to nitrites and oxidizes reduced methylene blue ( $\text{MBH}_2$ ) into methylene blue (MB):



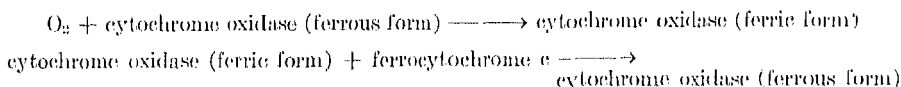
(c) *Azotase*, a system of enzymes present in *Azotobacter*, is active in nitrogen fixation. The amount of fixed nitrogen is proportional to the number of cells produced. The system or its components have thus far not been obtained in cell-free solutions. However, a hemoglobin-like protein has been isolated from the root nodules of leguminous plants forming a symbiotic union with nitrogen-fixing bacteria.

**DESMOLASES**

The desmolyzing enzymes are conveniently divided into three major groups: oxidases, dehydrogenases, and miscellaneous enzymes.

**Oxidases** (metalloproteins containing copper and iron) catalyze oxidation reactions in which molecular oxygen (but not hydrogen peroxide) is reduced. Their action is inhibited by hydrogen cyanide, hydrogen sulfide, and carbon monoxide. The best-known microbial oxidases are cytochrome oxidase, ascorbic acid oxidase, polyphenol oxidase, and luciferase.

(1) *Cytochrome oxidase*, produced by aerobic bacteria, yeasts, and molds, catalyzes the oxidation of ferrocytochrome c (reduced cytochrome) by molecular oxygen. It is hemoprotein in nature:



Cytochromes, the respiratory pigments, are iron-porphyrin proteins. Three cytochrome components (a, b, and c) are known, of which cytochrome c is the most stable. Some organisms lack cytochromes, and others have a modified cytochrome system: all aerobic organisms such as yeast and most molds contain cytochromes and cytochrome oxidase; facultative anaerobes may contain cytochrome; and anaerobes (such as *Clostridium butylicum*) have none.

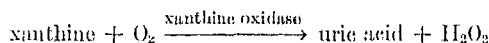
(2) *Ascorbic acid oxidase*, present in some intestinal bacteria, oxidizes ascorbic acid (vitamin C) to dehydroascorbic acid. It is probably a copper protein.

(3) *Polyphenol oxidase* (or *laccase*) and *monophenol oxidase* (or *tyrosinase*) are copper proteins that are widely distributed in nature and oxidize the corresponding compounds. They are elaborated by several yeasts and bacteria.

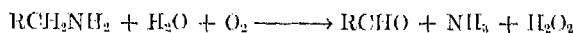
(4) *Luciferase* oxidizes luciferin (a substance of unknown composition) with the liberation of light. The process is called bioluminescence and is performed by luminous bacteria like *Achromobacter fischeri*. The optimum conditions for light production are 27°C. and pH 6-8. The enzyme has thus far been isolated only from the ostracod (*Cypridina*).

**Dehydrogenases** activate or mobilize hydrogen atoms of their substrates (donors) so that the hydrogen can be passed on to a reducible substance (acceptor). The mobilized hydrogen atoms may be transferred through a series of compounds until they are passed to final hydrogen acceptors. While oxidases can act only in the presence of molecular oxygen, aerobic dehydrogenases may pass the accepted hydrogen either to oxygen or to another substance. Dehydrogenases are named after the substance upon which they act and are divided into two major groups: (1) aerobic and (2) anaerobic dehydrogenases. Aerobic dehydrogenases transfer the activated hydrogen directly to oxygen, with the formation of hydrogen peroxide, while anaerobic dehydrogenases transfer the activated hydrogen to acceptors other than oxygen, such as cytochromes, coenzyme I, or coenzyme II.

(1) *Aerobic dehydrogenases* form hydrogen peroxide by transferring the activated hydrogen directly to oxygen. (a) *Xanthine oxidase* (or *Schardinger's aldehyde oxidase*) is known to catalyze the oxidation of at least thirty-five nontoxic aromatic and aliphatic aldehydes and nine purines related to xanthine and hypoxanthine:



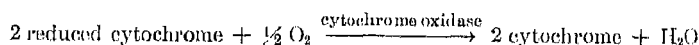
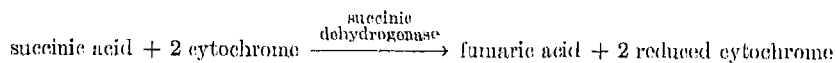
If no catalase (elaborated only by aerobic organisms) is present, the hydrogen peroxide formed will destroy the organism. The widely distributed enzyme, xanthine oxidase, is absent from yeast. (b) *D-Amino acid dehydrogenase* (*D-amino acid oxidase*) catalyzes the oxidation of natural amino acids with the formation of keto acids and ammonia. Only the first part of the reaction is catalytic: in the presence of a hydrogen acceptor, an imino acid ( $\text{RC}(:\text{NH})\text{COOH}$ ) is formed; this is then hydrolyzed with water into a keto acid and ammonia. The enzyme, a flavoprotein, is present in a number of microorganisms. (c) *Amine dehydrogenase* (*histaminase*) oxidizes amines into aldehydes with the formation of ammonia and hydrogen peroxide:



A number of organisms that may use amines as a source of nitrogen contain the enzyme. (d) *Uricase*, in the presence of air, catalyzes the conversion of uric acid to allantoin. The use of uric acid as the sole source of nitrogen is a favored test for identifying certain organisms; for instance, *Aerobacter aerogenes* utilizes uric acid, while *Escherichia coli* does not.

(2) *Anaerobic dehydrogenases* are divided into three classes: cytochrome-linked, coenzyme I-linked, and coenzyme II-linked.

*Cytochrome-linked dehydrogenases*: (a) *Succinic acid dehydrogenase* converts succinic acid to fumaric acid:

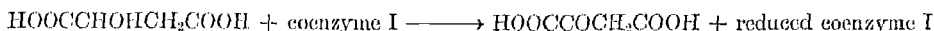


Instead of cytochrome, methylene blue may act as an acceptor of the hydrogen given up by the succinic acid. Succinic acid dehydrogenase, which is prominent in the  $\text{C}_4$  dicarboxylic acid cycle, has

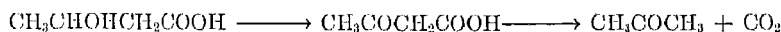
been found in some species of *Aspergilli*, in *Escherichia coli*, and in other organisms. (b) *Glycerophosphate dehydrogenase*, present in yeasts, catalyzes the oxidation of  $\alpha$ -glycerophosphate ( $\alpha$ -glycerophosphoric acid),  $\text{CH}_2\text{OHCHOHCH}_2\text{OPO}(\text{OH})_2$ , to 3-phosphoglyceraldehyde (glyceraldehyde 3-phosphate),  $\text{CHOCHOHCH}_2\text{OPO}(\text{OH})_2$ , thus playing a role in alcoholic fermentation. (c) *Lactic dehydrogenase* catalyzes the oxidation of lactic acid to pyruvic acid and the oxidation of  $\alpha$ -hydroxybutyric acid to  $\alpha$ -ketobutyric acid. The enzyme is found in yeasts, *Escherichia coli*, and other organisms. (d) *Formic dehydrogenase*, in the presence of an acceptor (methylene blue) catalyzes the oxidation of formic acid to carbon dioxide:



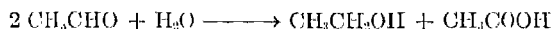
*Coenzyme I-linked dehydrogenases*: (a) *Lactic dehydrogenase*, in cooperation with coenzyme I, catalyzes the oxidation of lactic acid to pyruvic acid. The enzyme, present in *Escherichia coli* and *Aerobacter aerogenes*, differs from cytochrome-linked dehydrogenases by functioning with coenzyme I instead of cytochrome. (b) *Malic dehydrogenase*, also produced by *E. coli* and *A. aerogenes*, with the cooperation of coenzyme I catalyzes the oxidation of malic acid to oxalacetic acid:



(c) *Hydroxybutyric dehydrogenase*, functioning with coenzyme I, catalyzes the oxidation of  $\beta$ -hydroxybutyric acid to acetoacetic acid ( $\beta$ -ketobutyric acid), which then decomposes to acetone and carbon dioxide:

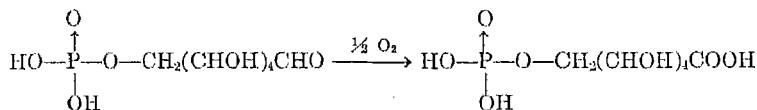


The enzyme is present in *Clostridium acetobutylicum* and takes part in the butanol-acetone fermentation (see p. 371). (d) *Glucose dehydrogenase*, in cooperation with either coenzyme I or coenzyme II, catalyzes the oxidation of glucose to gluconic acid,  $\text{CH}_2\text{OH}(\text{CHOH})_4\text{COOH}$ . Only D-glucose is acted upon. Several species of *Phytomonas*, *Pseudomonas*, *Aspergillus*, and others produce this enzyme. (e) *Alcohol dehydrogenase* catalyzes the oxidation of primary and secondary alcohols to aldehydes and ketones. The enzyme, present in yeast and other organisms, acts under both aerobic and anaerobic conditions. (f) *Aldehyde mutase* acts on two aldehyde molecules:

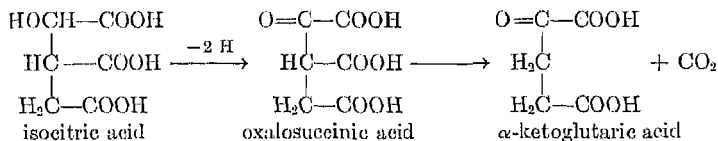


The enzyme, which is not identical with alcohol dehydrogenase or aldehyde dehydrogenase, is among the most important of the yeast enzymes. (g) *Triosephosphate dehydrogenase*, which catalyzes the oxidation of 3-phosphoglyceraldehyde into 1,3-diphosphoglycerate (glyceric acid 1,3-diphosphate), is present in yeast. (h) *Dihydroxyacetone phosphate dehydrogenase* catalyzes the formation of 3-phosphoglyceraldehyde from 1,3-dihydroxyacetone 1-phosphate,  $\text{HOCH}_2\text{COCCH}_2\text{OPO}(\text{OH})_2$ . (i) *L(+)-Glutamic acid dehydrogenase*, present in yeasts and in certain bacteria, in cooperation with coenzyme I (in higher plants) or coenzyme II (in yeasts) (see below), transforms L(+)-glutamic acid,  $\text{HOOC}(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{COOH}$ , to  $\alpha$ -ketoglutaric acid,  $\text{HOOC}(\text{CH}_2)_2\text{COCOOH}$ , and ammonia.

*Coenzyme II-linked dehydrogenases*: (a) *Hexose monophosphate dehydrogenase*, found in yeasts, catalyzes the oxidation of glucose 6-phosphate to 6-phosphogluconate (gluconic acid 6-phosphate):



(b) *Isocitric dehydrogenase*, in cooperation with coenzyme II, catalyzes the oxidation of isocitric acid to oxalosuccinic acid, which, by losing carbon dioxide, will yield  $\alpha$ -ketoglutaric acid:

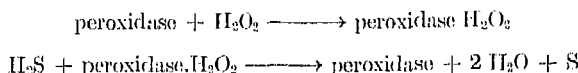


This important reaction forms a part of the so-called citric acid (*q.v.*) cycle, and the  $\alpha$ -ketoglutaric acid thus formed may be utilized in the production of glutamic acid by the microorganisms.



**Miscellaneous Enzymes:**

(1) *Peroxidases*, widely distributed in plant tissues, are common in many microorganisms; in the presence of hydrogen peroxide, they catalyze the oxidation of a number of substances:



The enzyme, cytochrome c peroxidase, which is present in yeast, is specific and catalyzes only the oxidation of reduced cytochrome c by hydrogen peroxide. Peroxidases are hemoproteins.

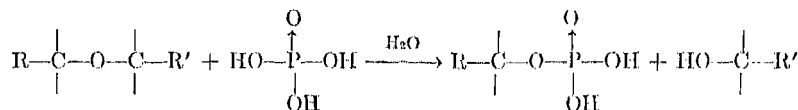
(2) *Catalase* is an indispensable constituent of every aerobic cell. It differs from the peroxidases by decomposing hydrogen peroxide into water and oxygen without requiring reducible substances to be present. All aerobic organisms produce catalase, while anaerobes do not. Catalase, which has a molecular weight of about 250,000, is a hemoprotein.

(3) *Carboxylases* catalyze the removal of carbon dioxide from various keto acids such as pyruvic acid or acetoacetic acid. (a) *Yeast carboxylase* is a diphosphothiamine magnesium protein (diphosphothiamine is the prosthetic group or coenzyme) and catalyzes the decarboxylation of pyruvic acid into acetaldehyde and carbon dioxide. The enzyme is a part of the zymase enzyme system. (b) *Aerobic pyruvic decarboxylase* catalyzes the oxidation of pyruvic acid to acetic acid and carbon dioxide. (c) *Anaerobic pyruvic decarboxylase* catalyzes the reaction:

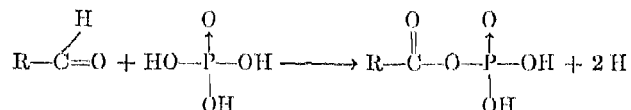


in which two molecules of pyruvic acid will yield acetic acid, lactic acid, and carbon dioxide by disproportionation. (d) *Acetoacetic decarboxylase*, present in *Clostridium acetobutylicum*, decarboxylates acetoacetic acid into acetone and carbon dioxide.

(4) *Phosphorylases* primarily catalyze reactions in which phosphate is added to organic compounds, a reaction called "phosphorylation." Polysaccharides or disaccharides are phosphorylated by the corresponding enzymes to yield glucose 1-phosphate, or Cori ester:

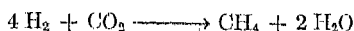


This reaction, which is analogous to the hydrolysis of higher carbohydrates, is essential to organisms that ferment disaccharides or carbohydrates of larger molecular weight. "Phosphorylative oxidation" is the addition of inorganic phosphate to compounds containing double bonds by simultaneous dehydrogenation of the substrate:



For instance, 3-phosphoglyceraldehyde may be oxidized to 1,3-diphosphoglycerate, one of the intermediate compounds formed during alcoholic fermentation. The phosphorylation reactions are reversible and also play an important role in the synthesis of higher carbohydrates.

(5) *Hydrogenase*, an enzyme produced by several bacteria, will reduce oxygen, methylene blue, nitrates, fumarates, sulfates, sulfites, etc., by "molecular hydrogen." A number of carbon-containing compounds such as carbon dioxide, carbon monoxide, formaldehyde, and methanol are reduced to methane. For example:



Hydrogenase, which works in cooperation with other enzymes that activate carbon dioxide to become a hydrogen acceptor, is found in *Escherichia coli*, *Micrococcus phosphoreus*, certain *Azotobacter* species, and other organisms.

(6) *Hydrogenylase* dehydrogenates formic acid:



where X may be methylene blue or an intracellular hydrogen carrier. Produced by *Escherichia coli* and other bacteria, the enzyme is adaptive and may be synthesized when formic acid is present in the medium, or is produced during the process of dissimilation.

(7) *Glyoxalase*, an enzyme widely distributed in various bacteria and yeast cells, catalyzes the intramolecular oxidation-reduction reaction of methylglyoxal to D-lactic acid, with the addition of one molecule of water. Glutathione is required for the reaction.

(8) *Racemase* (present in a number of bacteria like *Staphylococcus aureus*, *Clostridium butylicum*, and *Lactobacillus plantarum*) converts either D- or L-lactic acid into the racemic mixture.

(9) *Penicillinase*, the enzyme produced by several coliform bacteria and aerobic sporeforming rods, destroys penicillin.

(10) The *Zymase Complex*. "Zymase" is the classical name of the enzyme complex that catalyzes the fermentation in which ethanol and carbon dioxide are formed from hexose. Many of the individual components of this enzyme system have been mentioned on the preceding pages.

### Types of Controlled Microbial Actions

Microbial actions are grouped according to several systems, the following being the most frequent:

(1) According to the substrate, for example, fermentation of carbohydrates, proteins, or fats. Fermentation of carbohydrates, the most frequent and important, is usually further specified as cellulose, hemicellulose, starch, maltose, sucrose, fructose, glucose, etc., fermentation.

(2) After the name of the agricultural product or industrial by-product upon which the organism acts, as, fermentation of grains, potatoes, grapes, sugar-cane juice, cane-sugar molasses, sugar-beet juice, beet-sugar molasses, artichoke, dough, coffee beans, tea, flax, etc. Specific names are also given to some of these reactions, as, retting of flax, souring of cabbage, etc.

(3) According to the main compounds formed, as, alcoholic, butanol-acetone, lactic acid, butanediol, glycerol, etc., fermentation. "Fermentation of glycerol" means the breakdown of glycerol, which is carried out by many organisms, while "glycerol fermentation" usually refers to the formation of glycerol from sugars by microbial action.

(4) According to the operating technology, as, batch fermentations, semicontinuous fermentations, continuous fermentations.

(5) According to the absence or presence of air, as, "anaerobic" or "aerobic" process. Many aerobic processes are not true fermentations but are aerobic respiration, or biosynthesis.

(6) According to the principal type of enzyme action involved: *hydrolysis*, as the microbial hydrolysis of starch (conversion), of sucrose (inversion), of proteins (digestion, or autolysis if the cell uses its own substance as substrate), of fats (rancidification); *oxidation*, as the oxidation of ethanol to acetic acid; *fermentation*, as the transformation of glucose to lactic acid, to ethanol, and so on. A process producing vitamins, provitamins, growth factors, proteins, fats, toxins, or antibiotics is referred to as *microbial synthesis* of the corresponding substance (see also item 5 above).

(7) According to the origin and purity of the organism: pure culture fermentation (often incorrectly called sterile fermentation), when the sterilized medium in a closed container is inoculated with a pure culture; naturally pure fermentation (lactic acid, acetic acid), when the numbers of the desired organisms are overwhelming, and infections are suppressed merely by environmental conditions; mixed culture fermentation, in which more than one species of organism act on the substrate (Amylo process; see

TABLE I. Most Common Microbial Processes Used in Industry or Recommended for Industrial Application.

Manufactured product	Raw material	Compounds metabolized	Compounds formed	Type of microbial action	Microorganisms involved
<b>1. Industrial alcohol (see <i>Alcohol, industrial</i>)</b>					
(a).....	<i>P</i> : Molasses, sugar-cane juice, sugar-beet juice	<i>P</i> : Sucrose, invert sugar, raffinose	<i>P</i> : Ethanol, CO <sub>2</sub>	F	<i>P</i> : <i>Saccharomyces cerevisiae</i> , Rasse XII, Rasse II; <i>Sac. ananensis</i> , <i>Schizosaccharomyces pombe</i> —
(b).....	<i>A</i> : H <sub>2</sub> SO <sub>4</sub> , NH <sub>4</sub> salts, phosphates	<i>S</i> : Betaine, NH <sub>4</sub> compds., inorganic salts	<i>S</i> : Amyl, isoamyl, and propyl alcohols, glycerol, succinic acid, etc.	—	—
	<i>P</i> : Grains—corn, sorghum (milo), wheat, rye, barley	<i>P</i> : Maltose derived from starch	<i>P</i> : Ethanol, CO <sub>2</sub>	F	<i>P</i> : <i>Sac. cerevisiae</i> , <i>Sac. ananensis</i> , <i>Sch. pombe</i>
	<i>A</i> : Malt, molded bran, mold stillage	<i>S</i> : Organic and inorganic yeast nutrients	<i>S</i> : Amyl and isoamyl alcohols, glycerol, succinic acid, etc.	—	<i>A</i> : <i>Lactobacillus delbrueckii</i> , <i>Rhizopus japonicus</i> , <i>R. tonsuensis</i> , <i>R. delenar</i> , <i>Mucor rouxii</i> , <i>M. bouvard</i> , <i>Aspergillus oryzae</i> , <i>A. niger</i>
(c).....	<i>P</i> : Irish potatoes, sweet potatoes, dasheen	<i>P</i> : Maltose derived from starch	<i>P</i> : Ethanol, CO <sub>2</sub>	F	<i>P</i> : As for product (b) above
	<i>A</i> : Malt, molded bran, molded stillage	<i>S</i> : Organic and inorganic yeast nutrients	<i>S</i> : Amyl, isoamyl, and propyl alcohols, glycerol, succinic acid, etc.	—	<i>A</i> : As for product (b) above
(d).....	<i>P</i> : Manioc	<i>P</i> : Maltose derived from starch	<i>P</i> : Ethanol, CO <sub>2</sub>	F	<i>P</i> : As for product (b) above
	<i>A</i> : Malt	<i>S</i> : Organic and inorganic yeast nutrients	<i>S</i> : Amyl, isoamyl, and propyl alcohols, glycerol, succinic acid, etc.	—	<i>A</i> : As for product (b) above
(e).....	<i>P</i> : Jerusalem artichoke	<i>P</i> : Fructose derived from inulin	<i>P</i> : Ethanol, CO <sub>2</sub>	F	<i>P</i> : <i>Sac. cerevisiae</i>
	<i>A</i> : H <sub>2</sub> SO <sub>4</sub>	<i>S</i> : Organic and inorganic yeast nutrients	—	—	—
(f).....	<i>P</i> : Wood	<i>P</i> : Glucose	—	—	<i>P</i> : <i>Sac. cerevisiae</i>
	<i>A</i> : HCl, inorganic salts	<i>S</i> : Yeast nutrients	—	—	—
<b>2. Alcoholic beverages (see <i>Alcoholic beverages, distilled</i>)</b>					
(a) Wine ( <i>q.v.</i> )	Grapes, other fruit	Glucose, fructose	<i>P</i> : Ethanol, CO <sub>2</sub>	F	<i>Saccharomyces ellipsoides</i> , <i>Sac. pastorianus</i> (Tokay and Burgundy strains)
			<i>S</i> : Amyl, isoamyl, and propyl alcohols, glycerol, succinic acid, etc.		

(b) Beer ( <i>q.v.</i> ), ale	P: Malt, rice, corn grits, brewing sugar and sirups	P: Maltose derived from starch	P: Ethanol, CO <sub>2</sub>	F	P: <i>Sac. cerevisiae</i> , <i>Sac. carlsbergensis</i> , <i>Sac. monacensis</i> (bottom yeast), <i>Schizosaccharomyces pombe</i> (South African beer)
(c) Whiskey, and grain and potato brandies	A: Hops P: Corn, sorghum, wheat, rye, barley, Irish potatoes S: Malt	— P: Maltose derived from starch	— P: Ethanol, CO <sub>2</sub>	— F	— P: <i>Sac. cerevisiae</i>
(d) Fruit brandies	Wines made of any fruit	Glucose, fructose	Ethanol, CO <sub>2</sub>	F	<i>Sac. ellipsoideus</i>
(e) Rum	P: Sugar-cane molasses	P: Sucrose, invert sugar, raffinose	P: Ethanol, CO <sub>2</sub>	F	P: <i>Sac. cerevisiae</i> , <i>Schizosaccharomyces mellacei</i>
(f) Others: saké, arrack, etc.	S: H <sub>2</sub> SO <sub>4</sub> , inorganic salts Rice, cow milk, horse milk	— Starch, sucrose, glucose, fructose, raffinose	— Ethanol, CO <sub>2</sub>	— F	— <i>Schizosaccharomyces</i> and <i>Saccharomyces</i> spp., <i>Sac. japonicus</i> , <i>Aspergillus oryzae</i> , <i>Rhizopus</i> and <i>Mucor</i> spp.
3. Vinegar ( <i>q.v.</i> )	Wine, cider, beer, spirits	Ethanol	Acetic acid	F	<i>Bacterium curvum</i> , <i>B. orleanense</i> , <i>Acetobacter rancens</i> , <i>A. aceti</i> , <i>A. pasteurianum</i> , <i>A. xylinum</i> , <i>A. ascendens</i> , <i>A. acetigenum</i> , <i>A. melanogenum</i>
4. Lactic acid ( <i>q.v.</i> )	P: Corn, wheat, molasses	P: Lactose, maltose, glucose, sucrose, dextrins	P: Lactic acid	F	P: <i>Lactobacillus delbrueckii</i> , <i>L. bulgaricus</i> , <i>L. casei</i> , <i>L. leichmannii</i>
5. Butyric acid ( <i>q.v.</i> )	A: Malt, CaCO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> , malt sprouts P: Corn, potatoes, molasses A: CaCO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub>	— P: Starch, sucrose, invert sugar, calcium lactate	— P: Butyric acid, CO <sub>2</sub> , H <sub>2</sub> , acetic acid, etc.	— F	— P: <i>Clostridium butyricum</i>
6. Citric acid ( <i>q.v.</i> )	P: Sucrose, molasses	P: Sucrose, glucose, fructose	P: Citric acid	O	— P: <i>Citromyces pfefferianus</i> , <i>C. glaber</i> , <i>Aspergillus niger</i> , <i>A. clavatus</i> , <i>A. fumarius</i> , <i>A. aureus</i> , <i>Penicillium arena-rium</i> , <i>P. olivaceum</i> , <i>P. glaucum</i> , <i>P. luteum</i> , <i>Mucor</i> , <i>Ustilina</i>
	A: NH <sub>4</sub> salts, MgSO <sub>4</sub> , KH <sub>2</sub> PO <sub>4</sub> , HCl	—	S: Oxalic and gluconic acids	—	—

P = primary, S = secondary, A = auxiliary, F = fermentation, O = oxidative dissimilation (aerobic respiration), R = reproduction, G = growth, A = assimilation, B = biosynthesis, H = hydrolysis.

Continued

TABLE I. Most Common Microbial Processes Used in Industry or Recommended for Industrial Application (Continued).

Manufactured product	Raw material	Compounds metabolized	Compounds formed	Type of microbial action	Microorganisms involved
7. Gluconic acid (see <i>Sugar derivatives</i> )	<i>P</i> : Glucose derived from corn <i>A</i> : $\text{CaCO}_3$ , nutrient mineral salts	<i>P</i> : Glucose —	<i>P</i> : Gluconic acid —	O	<i>P</i> : <i>Aspergillus niger</i> , <i>A. fumigatus</i> , <i>Acetobacter aceti</i> , <i>Penicillium chrysogenum</i>
8. Fumaric acid (see <i>Maleic acid</i> )	<i>P</i> : Glucose derived from corn, molasses <i>A</i> : $(\text{NH}_4)_2\text{SO}_4$ , $\text{MgSO}_4$ , $\text{K}_2\text{HPO}_4$	<i>P</i> : Glucose, sucrose, invert sugar —	<i>P</i> : Fumaric acid, $\text{CO}_2$ —	O	<i>P</i> : <i>Rhizopus nigricans</i> —
9. Ethanol-acetone (see <i>Acetone</i> )	Potatoes, corn, molasses, hydrolyzed corn cob	Hexoses, pentoses, disaccharides, starch, pectin	Acetone, ethanol, $\text{CO}_2$ , $\text{H}_2$ , acetic acid	F	<i>Bacillus macerans</i> ( <i>B. acetohydrolicum</i> )
10. Butanediol (see <i>Glycols</i> )	<i>P</i> : Corn, wheat <i>A</i> : $\text{CaCO}_3$ , malt, $\text{H}_2\text{SO}_4$ , $(\text{NH}_4)_2\text{SO}_4$	<i>P</i> : Starch, dextrins, maltose, sucrose, glucose, fructose —	<i>P</i> : Butanediol, ethanol, acetoin, $\text{CO}_2$ , $\text{H}_2$ , acetone —	F	<i>P</i> : <i>Aerobacter aerogenes</i> , <i>Bacillus polymyxa</i> —
11. Compressed yeast (see <i>Yeasts</i> )	<i>P</i> : Molasses, malt, barley <i>A</i> : $(\text{NH}_4)_2\text{SO}_4$ , calcium superphosphate, malt sprouts, corn steep liquor	<i>P</i> : Maltose, sucrose, glucose, fructose, ethanol, $\text{NH}_4$ salts, phosphates, amino acids, peptone, etc. —	<i>P</i> : Bakers' or cake yeast, dried bakers' yeast <i>S</i> : Ethanol	R, G, A	<i>P</i> : <i>Saccharomyces cerevisiae</i>
12. Food and feed yeast (see <i>Yeasts</i> )	<i>P</i> : Molasses, sulfite liquor, stillage, waste brewers' yeast <i>A</i> : $(\text{NH}_4)_2\text{SO}_4$ , calcium superphosphate, malt sprouts, corn steep liquor	<i>P</i> : Maltose, sucrose, glucose, fructose, ethanol, $\text{NH}_4$ salts, phosphates, amino acids, peptones —	<i>P</i> : Yeast cells with high protein content —	R, G, A	<i>P</i> : <i>Saccharomyces cerevisiae</i> , <i>Torulopsis utilis</i> —
13. Glycerol ( <i>q.r.</i> )	<i>P</i> : Sucrose, molasses <i>S</i> : Malt sprouts, $\text{Na}_2\text{HPO}_4$ , $\text{MgSO}_4$ , $\text{NH}_4\text{Cl}$ , $\text{Na}_2\text{CO}_3$ , $\text{NaOH}$ , $\text{Na}_2\text{SO}_3$ , $\text{NaHSO}_3$ , $\text{CaO}$ , $\text{Ca}(\text{OH})_2$	<i>P</i> : Sucrose, glucose, fructose —	<i>P</i> : Glycerol, ethanol, acetaldehyde, $\text{CO}_2$ —	F modified by inhibitors —	<i>P</i> : <i>Saccharomyces cerevisiae</i> —

14. Antibiotics ( <i>q.v.</i> )	(a) Penicillin ( <i>q.v.</i> )	<i>P</i> : Lactose, corn steep liquor, stillage <i>S</i> : CaCO <sub>3</sub> , α-phenylacetamide nutrient supplements	<i>P</i> : Penicillin	B	<i>P</i> : <i>Penicillium notatum</i> , <i>P. chrysogenum</i>
	(b) Streptomycin ( <i>q.v.</i> )	<i>P</i> : Lactose, corn steep liquor, stillage <i>S</i> : CaCO <sub>3</sub> , nutrient supplements	<i>P</i> : Streptomycin	B	<i>P</i> : <i>Streptomyces griseus</i>
	(c) Chloromycetin ( <i>q.v.</i> )	<i>P</i> : Lactose, corn steep liquor, stillage <i>S</i> : CaCO <sub>3</sub> , nutrient supplements	<i>P</i> : Chloromycetin	B	<i>P</i> : <i>Streptomyces venezuelae</i>
	(d) Aureomycin (see <i>Streptomycin</i> )			B	<i>P</i> : <i>Streptomyces aureofaciens</i>
15. Fermented food and feed products (see <i>Food and food processing</i> )	(a) Sauerkraut	<i>P</i> : Cabbage	<i>P</i> : Lactic and acetic acids, mannitol, ethanol, CO <sub>2</sub> , esters	F	<i>P</i> : <i>Leuconostoc mesenteroides</i> , <i>Lactobacillus cucumeris</i> , <i>L. plantarum</i> , <i>L. pentosaceus</i> , <i>L. brevis</i> , <i>L. brassicae</i> , <i>Streptococcus lactis</i>
	(b) Pickles	<i>S</i> : Salt, dill, capers <i>P</i> : Cucumber	<i>P</i> : Lactic and acetic acids, etc.	F	<i>P</i> : Gram-positive cocci, short and long rods of <i>Lactobacilli</i>
	(c) Pickled green olives	<i>S</i> : Allspice, coriander seed, black pepper, dill, bay leaves, salt, lye, dextrose <i>P</i> : Olives (green)			<i>P</i> : <i>Lactobacillus pentosus</i> , <i>L. pentosaceus</i> , <i>L. brevis</i>
	(d) Silage (see <i>Feeds, animal</i> )	<i>S</i> : Dextrose Whole plant or stalk of corn, sorghum, sunflower, clover, alfalfa, pea, soybean, oat, rye, wheat, sugar beet, etc.	Lactic, acetic, propionic, and butyric acids, alcohols, esters	F	Bacteria ( <i>Lactobacillus</i> spp., <i>Streptococcus lactis</i> ), molds, yeasts

*P* = primary, *S* = secondary, *A* = auxiliary, *F* = fermentation, *O* = oxidative dissimilation (aerobic respiration), *R* = reproduction, *G* = growth, *A* = assimilation, *B* = biosynthesis, *H* = hydrolysis.

Continued

TABLE I. Most Common Microbial Processes Used in Industry or Recommended for Industrial Application (Concluded).

Manufactured product	Raw material	Compounds metabolized	Compounds formed	Type of microbial action	Mitroorganisms involved
(e) Fermented milk products (see <i>Dairy products</i> )					
(1) Buttermilk	Milk	Lactose	Lactic and acetic acids, etc.	F	<i>Streptococcus lactis</i> , <i>S. citro- rorus</i> , <i>Lactobacillus bul- garicus</i> , <i>L. casei</i> , <i>Saccharomyces kefir</i>
(2) Kefir	Milk	Lactose	"	F	<i>L. bulgaricus</i> and other <i>Lactobacilli</i>
(3) Yoghurt	Milk	Lactose	"	F	<i>L. casei</i> , <i>S. lactis</i> , yeasts
(4) Kumis	Milk	Lactose	"	F	<i>Penicillium roqueforti</i>
(5) Cheese	Milk	Lactose	Ketones, fatty acids	F	
16. Miscellaneous					
(a) Retting of flax and hemp	Flax, hemp	Hemicelluloses, galactans, mannans, pentosans, xylians, arabans	Galactose, mannose, xylose, arabinose, butanol, acetone, ethanol, acetic and butyric acids, etc.	H	<i>Clostridium butyricum</i> , <i>C. felsineum</i> , <i>Bacillus mucer- ans</i> , <i>Mucor stolonifer</i>
(b) Tobacco fermentation (see <i>Tobacco</i> )	Tobacco leaves	Sugars, cellulose, hemicellulose	—	F, O	<i>Bacillus polymyxa</i> , <i>B. my- coides</i> , <i>B. subtilis</i> , <i>B. mes- entericus</i> , <i>B. megatherium</i> , <i>Proteus vulgaris</i> , <i>Micro- coccus ceticus</i> , <i>Penicillium</i> and <i>Aspergillus</i> spp.
(c) Propionic acid ( <i>q.v.</i> )	P: Corn, sugars	P: Glucose, fructose, lac- tose, maltose, dextrin, starch, glycerol	P: Propionic and lactic acids, CO <sub>2</sub> , H <sub>2</sub>	F	<i>P: Propionibacterium freudenreichii</i> , <i>P. technicum</i> , <i>P. arabinosum</i>
(d) Leather ( <i>q.v.</i> )	A: (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , CaCO <sub>3</sub> Hides	Proteins, proteinaceous substances	NH <sub>3</sub> , CO <sub>2</sub>	—	—
(e) Bacterial ethanol fermentation (pulp)	Sugar solns., agave juice	Sugars	Ethanol, CO <sub>2</sub> , lactic acid, traces of glycerol, acetoin	H, F	<i>Bacillus erodens</i> , <i>B. mega- therium</i> , <i>Aspergillus oryzae</i> , <i>A. flavus</i> <i>Thermobacterium mobile</i>
(f) 1,2-Propanediol (see <i>Glycols</i> )	Rhamnosides	Rhamnose	Propanediol, CO <sub>2</sub> , H <sub>2</sub> , ace- tic and succinic acids	F	<i>Bacillus rhamnosifermen- tans</i>
(g) Cellulose decom- position and de- struction (see <i>Alcohol</i> , <i>industrial</i> )	Wood, flax, plant residues	Cellulose	(a) By anaerobic organ- isms: butyric and ace- tic acids, ethanol, methane, CO <sub>2</sub> , H <sub>2</sub> (b) By aerobic organisms: CO <sub>2</sub> , H <sub>2</sub> O	F	<i>Clostridium dissolens</i> , <i>C. cellulolyticum</i>
17. Vitamins ( <i>q.v.</i> )				O	<i>Polyporus vaporarius</i> , <i>Merulius domesticus</i>

*P* = primary, *S* = secondary, *A* = auxiliary, *F* = fermentation, *O* = oxidative dissimilation (aerobic respiration), *R* = reproduction, *G* = growth, *A* = assimilation, *B* = biosynthesis, *H* = hydrolysis.

Vol. 1, p. 259); spontaneous fermentation, in which the naturally occurring organisms initiate and carry on the fermentation of the media (a converted malt mash kept at proper temperature will undergo a lactic acid fermentation, as will milk, cucumber, and cabbage). Undesired organisms present in a fermentation are referred to as *infections* and the fermentation is called infected.

(8) According to the consistency of the fermenting substrate, the process is called liquid or solid. It is customary to distinguish between surface- and submerged-culture processes, depending upon whether the organism grows on the surface only or throughout the medium.

While microbial processes which occur in nature are incidental, those which are directed by human influence are controlled processes. The means of control characterize the industrial microbial processes, and patents are usually granted on the specification of the controls. Table I lists the most common industrial processes.

### Fermentation Technology

The knowledge of how to produce desired products from materials available in excess by the use of microorganisms was maintained as an art for thousands of years by generations of certain families. Today, it is a science in its own right, including other sciences such as bacteriology, biochemistry, physical chemistry, mathematics, and engineering, and is becoming known as "fermentation engineering." Research, development, production methods, production control, equipment design—as connected with industrial utilization of microorganisms—are all a part of fermentation engineering. The methods utilized by the fermentation industry generally include the following: selection of the raw materials, selection of the suitable organism, preparation of the raw materials, preparation of the inoculum, conduct of microbial action, recovery, and utilization of by-products

#### SELECTION OF MATERIALS

**Raw Materials.** Raw materials are commercially available substances that are changed into new products by the controlled action of microorganisms. They are either farm products (overwhelmingly of plant origin, occasionally of animal origin) or industrial by-products like molasses, sulfite liquors, corn steep liquor, stillage, and lactose. Fermentation industries, because they increase the value of excess farm products, originally were classified as agricultural industries, and the microbial processes were developed by agricultural chemists. (See *Cereals*; *Dairy products*; *Molasses*; *Pulp*; *Sugar manufacture*.)

Among *farm products*, fruit (grapes, apples, plums, cherries, apricots) is used to make wines and brandies. Grains (corn, rye, wheat, barley, sorghum (milo), rice) and tubers and roots (Irish potatoes, sweet potatoes, dasheen (taro), Jerusalem artichoke, sugar beets) are utilized chiefly to make industrial and beverage alcohol, butanol-acetone, lactic acid, compressed yeast, etc. Plants such as cucumbers, olives, cabbage, cornstalks, and beet leaves serve as the raw materials for pickled food and feed. Milk, cream, and casein are the raw materials for a great variety of food products prepared through microbial action. Among *industrial by-products*, molasses and sulfite liquors are the raw materials for industrial alcohol, compressed-yeast, and food-yeast production; bran, corn steep liquor, soybean cake, citrus fruit residue, whey, lactose, and stillage are raw materials for the production of antibiotics, enzymes, vitamins, and



growth factors. By-products of the meat industry like gelatin, scrap meat, liver, spleen, heart, and brain are used or recommended as raw materials in the microbial synthesis of vitamins and growth factors.

Low price, high yield, convenience in handling, possible year-round supply, close market, and purity are the main directives in selecting the raw material. Based on these points, different geographical locations favor different raw materials. In agricultural countries, corn is the most universal raw material for many processes; molasses is used close to sugar plantations or cheap water transportation; potatoes are utilized as seasonal products where they are grown in large quantities; rice is the raw material in the Orient; and manioc is used in South America. Grains are easily stored in silos and molasses in tanks. Tubers and roots must be used soon after harvest because they spoil easily in storage; they are considered seasonal raw materials and are used close to the place at which they are produced because their high moisture content will not permit their being transported.

In general, healthy, clean, raw materials, free from excessive microorganisms, are preferred. The processing of damaged, moldy, or decayed tubers and grains requires more attention and often special treatment. For producing foods and beverages in which the taste and aroma of the raw material will affect the final product, only specially selected, high-quality raw materials should be used.

TABLE II. Carbohydrate and Moisture Contents of Raw Materials Used in the Fermentation Industries.

Raw material	Moisture content, %	Carbohydrate content, %		Type of carbohydrate
		As is	Dry basis	
Of Plant Origin				
Sugar beets.....	76	17.5	72.92	Sucrose, fructose, glucose
Sugar cane.....	79.5	14	68.29	" " "
Grapes.....	65	22	62.86	" " "
Plums.....	70	18	60.0	" " "
Irish potatoes.....	76	20	83.33	Starch, traces of sugars
Sweet potatoes.....	62	26	68.42	Starch, sugars
Dasheen (taro).....	72	22	78.5	" "
Jerusalem artichoke.....	73	16.5	61.11	Inulin, fructose
Corn.....	13.5	58.5	67.63	Starch, traces of sugars
Rye.....	12.5	53.5	61.14	" " " "
Wheat.....	13.0	56.0	64.37	" " " "
Barley malt.....	6.0	50.0	53.19	Starch, sugars
Sorghum (milo).....	13.5	60.0	69.36	Starch, traces of sugars
Rice.....	13.0	76.0	87.36	Starch
Manioc.....	11.5	73.5	83.05	"
Of Animal Origin				
Cow milk.....	87.5	5.0	40.0	Lactose
Of Industrial Origin				
Cane molasses (blackstrap).....	20	62	77.50	Sucrose, raffinose, glucose, fructose
Beet molasses.....	20	50	62.5	" " " "
Sulfite liquor.....	91	2.5	27.8	Mannose, galactose, fructose, glucose
Corn steep liquor.....	50	0.0	0.0	" " " "
Grain stillage.....	97	0.5	7.1	Starch, dextrins, traces of glucose

The important components of raw materials are carbohydrates, proteins and other nitrogen compounds, phosphates and other inorganic salts, vitamins, and growth factors. Table II summarizes the approximate carbohydrate and moisture contents of the essential raw materials. Carbohydrates are dissimilated (fermented or oxidized) or assimilated. The carbohydrate content determines the yield, and hence, in most cases, the value of the raw material. The other constituents are mainly assimilated or used in biosynthesis. Some amino acids, through decarboxylation and deamination, yield fermentation products; isoamyl alcohol and amyl alcohol are formed from leucine and isoleucine, respectively (see p. 356).

The important *carbohydrates* are: starch in grains and potatoes; inulin in Jerusalem artichoke; glucose and fructose in fruits; sucrose, invert sugar, and raffinose in molasses; mannose and galactose in sulfite liquor; maltose in malt; lactose in milk and whey.

Among the different varieties of the same kind of grain on the market, those with the highest starch content are selected. Red winter wheat and Wisconsin rye are preferred. Barley varieties are the subject of constant selection by maltsters and brewers.

**Auxiliary Materials.** The substrate prepared for microbial processes often contains, besides the raw material, other substances referred to as auxiliary materials. Depending upon the purpose for which these are needed, they may be classified as: (1) diluting agents, (2) converting agents, (3) neutralizing and pH stabilizing agents, (4) microbial nutrients, (5) activators, (6) antiseptics, (7) taste and aroma providers.

(1) The *diluting agent* is most frequently water. Microbial processes are conducted in aqueous media, as solutions, suspensions, semisolid media, or humidified solid media. The quality and quantity of dissolved and suspended substances, the natural content of microorganisms, and, in many cases, the odor and taste of the water are essential. Breweries and distilleries usually are located where a good and ample supply of water is available all year around. Besides natural water, industrial products like wine, dilute spirits, dilute vinegar, stillage, and whey are occasionally used as diluting agents.

(2) By predigesting the complex components, *converting agents* make some raw materials available for microbial action. Converting agents are biochemical catalysts (enzymes) or purely chemical catalysts, and they catalyze the hydrolysis of complex carbohydrates, proteins, and other substances.

In the production of alcohol, the starch content of grains, potatoes, manioc, and other raw materials must be converted (hydrolyzed) to maltose or dextrose, and the raffinose and sucrose content of molasses is advantageously converted to glucose, fructose, and galactose. Starches are preferably converted by malt amylase; malt is primarily made of barley, occasionally of rye and wheat, seldom of corn or other grains; 6-10 parts of barley malt is used to convert 100 parts of corn or rye. For making beer, barley malt is not only a converting agent but also the chief raw material. Microbial (fungal) amylase, which in recent years has found industrial application, can be used when malt is not available or is too high in price. Inorganic acids (hydrochloric and sulfuric) are seldom used to convert starch, but sulfuric acid is frequently employed in hydrolyzing the sugars of molasses, and hydrochloric acid in hydrolyzing the cellulose of woods.

(3) *Neutralizing agents* reduce the excess acidity or alkalinity and help to establish and maintain the required pH in the substrate. Excess acidity may originate from the raw material, from the acids used for hydrolysis, or from the nutrient ingredients added to the substrate, or it may be produced from carbohydrates by the microorganisms. Lime or a calcium hydroxide slurry, calcium carbonate (in the form of ground limestone

or in the form of precipitated calcium carbonate), caustic soda, sodium carbonate, and ammonium hydroxide are commonly used to neutralize acids. Lime or calcium carbonate is applied to neutralize sulfuric acid after hydrolysis is completed; it is also added to the fermenting mash in lactic acid, butanol-acetone, gluconic acid, oxalic acid, 2,3-butanediol, penicillin, and streptomycin production. Caustic soda and sodium carbonate are common agents for neutralizing acid-treated molasses, and ammonium hydroxide is added to the wort in yeast production (where it also serves as nitrogen nutrient).

Excess alkalinity may originate from the raw materials (beet molasses are alkaline), from the diluting water (some well waters are alkaline), from alkali treatment of the media, and from metabolic bases, like ammonia, produced by microbial deamination. Alkalinity is counteracted by the addition of sulfuric, phosphoric, lactic, or other acids. (For such purpose, lactic acid occasionally is produced by means of fermentation in a separate fermenter; such fermentations are called "auxiliary fermentations.")

(4) *Microbial nutrients* are the compounds of the substrate that are assimilable by the organisms. Often the raw material contains sufficient nutrients: grains, for example, are high enough in proteins and proteinaceous substances, mineral components, and growth factors so that the addition of supplements to grain mash is unnecessary. When propagation of the organism is the main purpose or its development is important, added ingredients (supplements) play an essential role. In the manufacture of yeast, molasses supplemented with ammonium and phosphorus salts yields five times more yeast than molasses without the nutrient salts. For the majority of raw materials, the most needed supplements are the nitrogen and phosphorus compounds. Nitrogen is usually provided in the form of liquid ammonia, ammonium salts, urea, amino acid, protein hydrolyzates, and, rarely, nitrites or nitrates; phosphorus is added in the form of calcium superphosphate, ammonium phosphate, or alkali phosphates. To substrates low in carbohydrates, sugars are added. Lactose, in crystalline form, is a frequent supplement for corn steep liquor or grain stillage mash for antibiotics. Trace quantities of other elements, like manganese, iron, cobalt, nickel, zinc, and copper, needed in the synthesis of enzymes and growth factors, are often added in the form of salts. The addition of vitamins, vitamin precursors, or precursors of antibiotics to the medium is also customary.

(5) *Activators*, substances which in minute quantities mixed in the substrate will accelerate the microbiological process, are of two kinds:

(a) The first type are the trace elements, vitamins, growth factors, and precursors of vitamins necessary for speedy synthesis of enzymes or to counteract the action of inhibitors such as antivitamin if present in the medium. Yeast extract, wheat or rye bran and their acidic or alkaline decoctions, and malt sprouts are commonly used as activators, in addition to being nutrients.

Auxiliary microbial action sometimes results in the production of biologically active compounds. Yeast, for example, is often propagated in grain mash in which *Lactobacilli* were grown previously. Residues of alcoholic fermentations are added to the media in which antibiotics are produced to activate the growth of the organism and the biosynthesis.

(b) The other kinds of activators take no part in metabolism, but accelerate microbial actions by offering a large surface area. For example, activated carbon added to the beer when making ethanol may reduce the normal fermentation time by

50%. Asbestos, small paper slips, ground straw, and other inert substances with large surface areas have been shown to accelerate the butanol-acetone fermentation of clear solutions of sugars and nutrients.

(6) *Antiseptics* are occasionally added to a substrate in order to protect the principal organisms from undesired infections that are competing for the nutrients. For instance, yeast (after several generations) can become acclimated to small quantities of sulfuric acid, lactic acid, and fluorine compounds ( $\text{HF}$ ,  $\text{NaF}$ ,  $\text{KF}$ ,  $\text{NaHF}_2$ )—compounds that are used to prevent infections by bacteria, etc. The acclimated yeast then can propagate and ferment without interference. It is also customary to acidify the wine, cider, or dilute alcohol with acetic acid before the oxidation of the alcohol content to vinegar. Added acetic acid will aid the *Acetobacter* against contamination. The initial addition of a small amount of lactic acid to a mash subjected to lactic acid fermentation will help to maintain the purity of the bacteria involved in the fermentation.

(7) *Taste and aroma providers*. Salts and spices are often mixed with substrates from which a food or beverage is produced by microbial action. Salt is added to cabbages, cucumbers, or olives before they are subjected to lactic fermentation, and to the curd in cheese before the aging process. Flavor-providing botanicals, like wormwood and wild cherry, are added to grape juice to give the desired character to special wines. Peat smoke provides the characteristic aroma of Scotch whiskey.

#### SELECTION OF THE SUITABLE MICROORGANISM

The term "suitable" limits the choice of a microorganism not only to one capable of effecting the reaction wanted but to one that can effect the desired biochemical change within a short time and can produce the highest possible yield with a minimum of attention. The proper organism is also able to maintain its activity from generation to generation and to combat infections. Cultures of bacteria, yeasts, and molds used in established processes are usually available from scientific culture collections such as the A.T.C.C. (American Type Culture Collection, Georgetown University, School of Medicine, Washington, D.C.), the Collection Center of Microbic Types (Avenue César Roux 19, Lausanne, Switzerland), the collections of the various universities, and the Regional Research Laboratories of the U.S. Department of Agriculture. Individual strains most suited for special processing arrangements, and selected with much care, are kept in the collections of the manufacturers, but in these cases usually both the cultures and their specific properties are kept confidential. While many strains of a species do not answer all the requirements for a particular process, it is usually possible to find, acclimatize, mutate, or "breed" specific strains with suitable qualities. Some strains of *Penicillium chrysogenum*, for instance, under identical conditions produce one hundred times more penicillin than do others. Special strains of *Saccharomyces ellipsoideus* (wine yeasts) tolerate and produce 20% alcohol, while others cease fermenting in the presence of 12–14% alcohol.

The organism is first grown and studied on a small scale on the surface of or inside a solid medium and on the surface or on the bottom of unshaken liquid media. The clustering of a number of cells into a visible unit is called a "colony," and it bears an appearance characteristic of the species. The colony of a multicell organism may be represented by a single individual while that of a monocelled organism (yeast, bacteria) may comprise billions. A "culture" is the result of the growth of an organism on or in a laboratory medium, usually in a closed container, test tube, or propagating flask, protected from contaminants. Cultures and colonies are broadly utilized in microbial processes and their

growth characteristics and biochemical activities are studied and described as for one unit. In fact, the biochemistry of one monocellular individual, because of its size, cannot be studied at all.

Since in most cases the speed and completeness of a desired microbial action are in proportion to the quantity of organisms present, the reproduction of microorganisms is an essential part of almost every microbial process. Some microbial cells reproduce by fission (splitting the cells), some by forming buds or sprouts that will grow until they reach the size and maturity of the mother cell, and others both ways. Many organisms, besides reproducing by cell division, may form special reproduction bodies, commonly called spores, which, under favorable conditions, may also develop into new individuals. The manner of reproduction of a microbial cell is characteristic of the species.

The quantity of bacteria and yeasts is expressed by the number of cells per milliliter of medium. This is a rough type of estimation because the weight of well-developed cells of the same species might be two or more times that of smaller ones. Specifying the dry weight of the organisms in grams per 100 ml. of medium is more exact. Under suitable conditions, microorganisms can populate a medium very quickly. One single bacterium in 24 hours in a favorable environment may reproduce into  $2^{24}$  new individuals. After a few hours' incubation time, 1 ml. of an inoculated industrial beer will contain 1-200 million yeast cells. A mold 100 square microns in size may grow to 500 million square microns overnight.

Usually hundreds of strains of an organism isolated from natural sources or obtained from mutations of a mother culture are tested on small scale before the best-suited ones are taken into industrial use. In developing cultures to do a desired job, the most successful methods employ acclimatization, cultivation on alternating media, shock, hybridization, and the development of mutants. By being exposed to changes in the media or in the environmental conditions, in a series of consecutive cultivations, some organisms can develop adaptation to conditions considered most desirable by the manufacturer, for example, a special temperature, pH, or concentration, or to a specific carbohydrate, antiseptic, etc. The process is called *acclimatization*. Activity is maintained, or lost activity is regained, for many microorganisms by *cultivation on alternating media*. Butanol-producing bacteria, for instance, are usually grown for 2 days on rice paste supplemented with yeast autolyzate and then for 2 days on potato paste supplemented with alkaline extract of rye bran. To maintain their activity, many yeasts and molds grown on solid or semisolid media are transferred to liquid media for every other generation. Some sporeforming organisms regain lost activity if allowed to sporulate at intervals. *Shock* is a radical change in environment to which the organism is exposed for a short time. Examples are a strong acid treatment, a sudden change in osmotic pressure, or exposure for a few minutes to high temperature. When yeast is separated from the medium on which it is cultivated, it is washed with water, with a change in osmotic pressure. This yeast, which is used for seeding in, for example, the production of bakers' yeast, is often suspended in a 1-2% sulfuric acid solution for a few minutes before use as inoculum (seed); the result is an increased propagating activity and the lowering of the autolytic tendency of the cells. In butanol-acetone fermentations, the test tube containing the culture of *Clostridium acetobutylicum* is placed in boiling water for 2 minutes before transfer of the bacteria into a new medium; this heat shock maintains and/or increases the fermenting activity of the subculture.

*Mutants* are the cultures derived from a cell or cells possessing different properties than those of the mother culture. Mutation in a culture may occur accidentally, without external interference, but can be initiated by severe treatment, such as exposing the organism to short waves, ultraviolet or infrared rays, and radioactive radiations. The offspring of some cells isolated from such a treated culture exhibit mutation, that is, a permanent change in one or more characteristics from those of the mother culture. The mutants may be superior or inferior to the mother culture with respect to the desired qualities. When the mutant shows superior properties, the best-suited strain is then chosen for making the inocula.

#### PREPARATION OF RAW MATERIALS

Most raw materials, before being exposed to microbial action, must be subjected to physical and/or chemical treatments in order to obtain a substrate most suited to the organism and the processing conditions. Soluble raw materials like molasses, sugars, and sirups are dissolved in hot water. Sugar-containing, soft, plant parts like fruits (grapes, apples), tubers (sugar beet), or stems (sugar cane) are crushed or sliced;

often the juice is separated by pressing the crushed parts, and the solid residue is extracted by water. Soft plant parts containing starch (various potatoes) are cooked either at atmospheric or at superatmospheric pressure in order to break the starch-containing cells and pastify the starch. Grains (all of which contain starch) first are ground and then cooked with water; in Europe, they are cooked in special containers (*Henzedampfers*) without grinding. For special purposes (butanol-acetone, 2,3-butanediol by *Bacillus polymyxa*, butyric acid, the Amylo process) the cooked starchy paste in proper dilution constitutes the mash, but for most processes the starchy paste is first converted into fermentable sugars. Many manufacturing methods are satisfied by a substrate containing the undissolved plant residue suspended in the solution of the carbohydrates and nutrients, as in the processes of making grain and potato alcohol, fruit brandies, lactic acid, and 2,3-butanediol by *Aerobacter aerogenes*. Others require as substrate a clear liquid containing only dissolved substances, as fruit juices for making wines, wort for making beer, solutions of molasses or clarified grain wort for making compressed yeast, and synthetic broths for making antibiotics.

Grinding is performed by roller mills, attrition mills, or hammer mills, crushing by fruit crushers, slicing by slicers.

Cooking is carried out in agitated tanks heated with direct steam. Cooking at atmospheric pressure is performed in open tubs, and at elevated pressure in closed steel tanks called "cookers." Occasionally continuous cookers or the fermenters are used for cooking.

Clear liquids are obtained by pressing the crushed plant parts (the solid residue acts as filtering material), by filtering the converted grain mash through the grain residue in a perforated-bottom tank (malt hulls act especially well as filters), or by centrifuging the liquid (as are molasses solutions in compressed yeast production). Liquids are occasionally filtered through special filters. A clear solution (broth) is also obtained by dissolving soluble ingredients like molasses and inorganic salts, or crystalline sugars and soluble nutrients. Clarification is often needed to obtain sparkling, clear liquids; it is accomplished either by addition of a small amount of insoluble, large-surfaced material or by production of a precipitate. Fuller's earth, various filter-aids, and asbestos are frequently used as clarifiers; albumin, calcium sulfate, and calcium phosphate are common clarifying precipitates. The suspended solid, after adsorbing on its surface the fine floating particles, is then separated by sedimentation or centrifuging.

pH adjustment of the substrate to an initial optimum before inoculation by microorganisms is part of the preparation of the raw materials. The initial optimum pH depends upon the organisms used, the reaction desired, and the process employed. Molds adapt themselves easily to large pH variations: some grow within a pH range of 2-7; others, however, prefer high acid concentration; and others prefer highly alkaline media. In the production of citric acid with *Aspergillus niger*, the pH is set to 2 or less; in the production of gluconic acid, to 3.5; and in the production of fungal amylase, to 5 or above. The pH of the liquid for bakers' yeast is 5.5-6.5; but, when fermenting sugars by the same organism (*Saccharomyces cerevisiae*), the pH is 4.5-5.0. If it is possible to maintain the initial pH through the process, it is set exactly at the optimum; but, in processes without control, the pH is set more nearly neutral than the optimum. Because of the dominating influence of the pH on the success of microbial processes, buffers such as phosphates, amino acids, and protein hydrolyzates are often added to a medium. In alcohol production, it is a general practice to add

spent beer (stillage) to the beer (usually one-fourth to one-third of total volume) as a pH stabilizer as well as a yeast nutrient.

The optimum *initial temperature* depends upon factors similar to those that control the pH. While most organisms tolerate wide temperature ranges, optimums exist for both growth and the enzymic action. Frequently, they are identical or close together, and, occasionally, they are a few degrees apart. Usually, a shift in temperature will shift the proportion of dissimilation products. If provision is made to conduct away the heat generated during the microbial process, the temperature of the medium is set to optimum before inoculation, but it is set below optimum if the cooling device is inadequate or absent. In alcohol production, the beer is inoculated at 84–86°F. in fermenters with a perfect cooling system, at 78–80°F. if the cooling device is inadequate, and at 68–72°F. in fermenters having no coolers.

Since during the process of preparation most raw materials are heated, cooling is necessary to bring the substrate to the setting temperature. Cooling is accomplished by (a) evaporation at low pressure (barometric cooling), (b) cold water or, infrequently, brine circulated in heat exchangers (coils, plate coolers, etc.), (c) dilution of the liquid with cold water or cold stillage, or (d) a combination of the three methods.

A few processes require complete or partial *sterilization of the raw material*. Complete sterilization usually is effected during or after preparation of the material by heating the substance in a closed apparatus to a temperature at which all microorganisms and their spores are destroyed. Clear solutions, in which heat transfer is good, are sterilized with relative ease; exposure to 120°C. for 15 minutes is usually sufficient. Sterilization of liquids containing undissolved particles, such as unfiltered grain mashes and grain stillages, is difficult or often impossible without damaging the substance. Sterilization of the medium used for making the inoculum is standard practice in most commercial processes. In pure-culture processes, the substrate is always sterilized, and quite frequently this is performed in the fermenting tanks. Yeasts, molds, and their spores are normally destroyed within a few minutes at 80–90°C., but several bacterial spores resist temperatures above 100°C., and either long treatment (2–3 hours' cooking at 110°C.) or high temperature (125–130°C. for 15 minutes) is necessary to destroy them.

Heat usually is supplied by introducing live steam into the liquid or into the closed chamber containing the substance. Occasionally, heat exchangers are employed. Heat transfer is poor in starch pastes and thick mashes. The most promising method of sterilizing pastes and liquids containing undissolved particles is heating by high-frequency electricity; for this purpose, the substance, in a container that will not conduct electricity (glass), is placed between the electrodes, and heat is generated in the substance. Heat sterilization is more successful at low or high pH values; in most commercial methods, heat is applied at the lowest pH that can be permitted, and the pH is readjusted, if necessary, after sterilization.

Partial sterilization of the raw material is accomplished by exposing it to 80–100°C., at which temperature the vegetative cells of all organisms are killed. In the pasteurization usually applied to milk and cream, the substance is exposed to the minimum heat treatment sufficient to destroy all pathogenic bacteria: 60°C. for 20–30 minutes, or 80–85°C. for 1 minute or less, are the temperatures commonly used. Intermittent (or fractional) sterilization is often practiced in sterilizing laboratory media for inocula. It consists of three subsequent partial sterilizations, each 1 day apart or with a 2-day waiting period between the second and third partial sterilizations. Spores

not destroyed by the first or second partial sterilization thus have an opportunity to germinate, producing vegetative cells of that form which are destroyed by the later heating. Ultraviolet radiation has been applied as a means of sterilizing clear liquids. The addition to the media of chemicals that inhibit the growth of undesired organisms is an old practice: tartaric acid in fruit juices and lactic acid in dough and yeast mash permit the growth of yeast while preventing the development of undesired organisms. Fermentation as well as spoiling of fruit juices is frequently prevented by the addition of sulfur dioxide, which is eliminated from the medium before inoculation by heat, precipitation, or aeration; by this treatment, the liquid becomes partially sterilized.

On a laboratory scale, the medium used for anaerobic processes usually is corrected for *oxidation-reduction potential* by the addition of compounds like cysteine, methionine, and ascorbic acid. In the plant, however, the oxygen tension is reduced by boiling out the air from the substrate during the final sterilization, as in the preparation of raw material for the butanol-acetone fermentation.

*Dilution of the substrate*, that is, the exact setting of the proportion of solids to the water, is an essential operation. The limiting factor is usually the carbohydrate content, occasionally the ash content, and infrequently the protein content of the raw materials used. Dilution is governed by the need to obtain the products at the highest possible concentration for economy of fermenter space and recovery expense. The upper limit of concentration is determined by the tolerance of the organisms to the initial carbohydrate concentration (or concentration of other substances present) and to the final concentration of the end-products or by-products. If the raw material is too concentrated, the microbial process is slow or incomplete. Mashies made from molasses or grain in alcohol production are diluted to yield 7–12% alcohol, while mashies in butanol-acetone production are diluted to yield 3–3.5% solvents by volume; the liquid used in citric acid production usually is set to 15 grams sucrose per 100 ml.; lactic mash yields a 12–14% solution of calcium lactate; and the alcoholic solution in vinegar production is controlled to yield 10–12% acetic acid by volume.

In making solutions from solids or sirups, the water is added in several portions, control of the amount added being based either on the final specific gravity of the liquid or the ratio of weight of material used to final liquid volume in the fermenter. In preparing beer for alcohol production, with each bushel of ground grain (56 lb.) about 20 gal. of water is added in the cookers. After cooking, this will result in about 28–29 gal. cooker mash. The 8–10 gal. stillage and about  $\frac{3}{4}$  gal. yeast added with this cooker mash to the fermenter yield about 36–40 gal. beer per bushel of grain.

#### PREPARATION OF INOCULUM

The inoculum is any amount of living organisms (vegetative cells or spores), with or without the medium in which it developed, that serves as a starter for a newly prepared (sterile or unsterile) substrate. The organisms will grow in or on the substrate and catalyze a desired biochemical change.

When the number of added organisms is large enough to carry out the biochemical change without additional growth, the organism is referred to as a "fermenting agent" or "biocatalyst" but not as an inoculum. In the Boinot process, the total amount of yeast separated from a fermented beer is added as a starter to the next batch of equal size. In the deep-culture citric acid process, the total of the mold mycelia is re-used several times in consecutive batches. In these instances, the yeasts and the mold body are fermenting agents and not inocula.



Inocula must be able to propagate fast and to complete the desired microbial action within a limited time. They are prepared in many ways and are of different types. Inocula for the final commercial batches are usually produced in several consecutive cultivation stages, beginning with a test-tube culture. (a) The original culture, grown in a test tube on a medium best suited to the particular organism, is called the "master culture"; equally ranked subcultures of master cultures, developed under identical conditions, are kept in a refrigerator at around 4°C. and are used as starters when needed. (b) Usually, the culture grown in one test tube is transferred to 500–2000 ml. of sterile medium, where it is permitted to grow before (c) transfer into 5–50 gal. of nutrient solutions. (d) In each subsequent transfer, as a rule the amount of inoculum transferred to the new medium is that necessary for approximately maximum growth within an incubation time of 12–24 hours for submerged media, and within 48–96 hours for surface growth. (Organisms needing air grow on the surface of media; those functioning anaerobically grow below the surface, that is, submerged.)

Preparation of the inoculum is also considered as divided into three phases, based primarily on the quantities involved: the laboratory, the intermediate, and the industrial stages. In the first two stages, the amounts of the cultures are negligible, and the nutrient solutions are more expensive and are always sterilized before inoculation. In the industrial stage, the culture is propagated in a nutrient having a composition close to that of the final mash, often under semipure conditions, that is, in medium that has been pasteurized but not sterilized. Cultures in quantities less than 2 liters are considered to be "on laboratory scale." In general, cultures larger than 2 liters but less than 50 gal. are considered as inocula in intermediate stages, although less than 50 gal. may constitute the final inoculum in some instances. It is customary to prepare inocula in several equally ranked, parallel-sized propagating tanks in the final stage instead of as one large batch; the medium for the last growth is prepared mainly from the raw material of which the final mash is made.

In each phase (laboratory, intermediate, and industrial), the inoculum may be transferred to increasing volumes of nutrients one to three times. For instance, in the laboratory phase, most inocula are cultivated in three steps: as noted above, the master culture is generally grown in a test tube on an agar medium; in the second step, the culture is propagated in 10–500 ml. of medium placed in test tubes, Erlenmeyer flasks, Florence flasks, Roux bottles (flat bottles), and like devices; in the third step, the culture is transferred into 200–2000 ml. of medium enclosed in a suitable container. Usually the entire contents of a flask is transferred to a second flask or container containing five to fifty times more sterile nutrient, although one culture may be divided among two or more flasks if needed.

Quantities up to 2–5 gal. are prepared in glass containers and quantities above that in well-constructed, tin-coated, copper or stainless-steel propagators.

It is also customary to prepare a larger number of the smaller-sized cultures and to use only the best ones. The cultures are classified for this purpose by experienced technicians by macroscopic, microscopic, and/or chemical investigation. Gas formation, proper development of mold spores, and cloudiness of the originally clear medium can be seen by the naked eye; the purity of the culture, cell size, and cell population, by microscope; and acid formation, by titration, etc.

The medium may be solid (like agar, gelatin, starch paste, grainpaste, or moistened bran), semisolid (a liquid medium with 0.5–0.75% agar), or liquid (either filtered or containing suspended solids). *Yeasts* and *bacteria* usually are propagated in liquids.

After being grown on agar surfaces in flat bottles, the cultures are suspended in saline solution or broth before transfer to the nutrient liquid. Bacteria are often grown in thin starchy pastes (the paste is liquefied, during propagation, by a bacterial amylase). *Molds* are cultivated for spore production on solid media, and for mycelia production in liquids.

It is not wise to economize on the size of inoculum at the expense of prolonging the final incubation period. Because processing time must be kept at a minimum and production capacity must be kept high, the inoculum is applied in slight excess. The number of transfers made between the test-tube culture and the final inoculum is kept as low as possible in order to reduce excess work and chances for contamination. However, for the reason of economizing on the expensive nutrients used in the earlier transfers, inocula are frequently produced in more steps than the possible minimum. Frequently, batches of final inocula are not the direct result of cultivation from separate test-tube cultures. For example, in alcohol production, the daily nutrient in which the yeast inoculum for the final mash is to be raised is inoculated with a portion of the inoculum set the previous day. Fresh yeast is made from a test-tube culture only once a month or once a year. Continuous fermentation processes need the minimum amount of inoculum constituting one starter to be used at the beginning of a production season.

Depending upon the kind of organisms and type of process, the quantity of final inoculum may amount to from 0.1 to 25% of the new substrate: 1 gal. of lactic acid culture added to 1000 gal. of malt mash will result in maximum growth in 16 hours' time; 2 gal. of yeast added to 100 gal. of grain beer will reach a maximum cell count in 16 hours; and 2 gal. of *Clostridium acetobutylicum* inoculum in 1000 gal. of corn mash approaches maximum cell population in 20 hours. In bakers' yeast production, the cells of the inoculum (called seed yeast or mother yeast) are grown in each fresh medium long enough to produce 5 to 10 new cells before being separated from the exhausted nutrient liquid. When mold spores are used as inoculum, the number of spores added per liter of medium is often the mode of describing the dosage; a common starter contains 1-20 million spores per 1000 ml. of medium.

#### CONDUCT OF MICROBIAL ACTIONS — FERMENTATIONS

The most important phase of the industrial process using microorganisms is the microbial action itself, commonly termed "fermentation." Regardless of the type of method applied, the success of such processes depends upon the control of several important factors. The most important are: the initial and final values; the variations, during processing, of convertible substances (usually carbohydrates), assimilable (nutrient) substances, temperature, pH, titratable acidity or alkalinity, and converted (final) products; and the amount of microorganisms functioning at any time during the fermentation.

**Systems.** In typical *batch systems*, the concentration of the convertible substance is reduced gradually from a relatively high initial value to a final minimum, while the value of the product is increased gradually from a minimum (almost zero) value to a maximum. At the same time, the amount (size and/or number of cells) of organisms increases from an initial minimum to a maximum and then decreases slightly or stays at the maximum until the end of the microbial action. Thus the behavior of all three factors—substance, product, organisms—follows more or less along logarithmic lines,

the main fermentation phase falling on the sloping part of the curves. During this phase, the changes per minute are often many hundred times greater than during the initial or end phase. In the batch system, not only do the values of the "three" change according to standard curves, but the speed of the changes follows a known relationship with time. It is characteristic of batch systems that the speeds of transformation at the beginning and at the end of the process are very slow, and that the whole process thus requires considerable time. One-half the total sugars is often fermented within 8–10 hours (during main fermentation period) of a fermentation process lasting 60–70 hours.

In the practical execution of a batch process, the prepared raw material is seeded with a small amount of inoculum, and the organisms begin to propagate and convert the substrate with increasing rate. After the rate of conversion reaches a maximum, it becomes close to constant for a short time; then, with the gradual disappearance of the convertible material and the gradual accumulation of the product (inhibiting microbial action), the rate of conversion gradually slows down to zero.

In typical *continuous systems*, the value of the "three" in the reaction vessel (fermenter) is kept more or less constant; consequently the speed of raw material transformation (assimilation, dissimilation, or biosynthesis) becomes constant, and the speed of changes is nil. By utilizing the almost maximum speed throughout, continuous processes may transform two to three times more raw material than a batch process does in the same-size processing (fermenting) tank. No time is lost by charging, discharging, and cleaning. Added advantages are the need for less frequent inocula, reduced manual labor, and less supervision.

Several microbial methods, however, cannot be carried out successfully in continuous processes. Major difficulties are the prevention of infections, degeneration of the organisms, and differences in optimum pH values of parallel-acting enzymes. While the continuous alcoholic fermentation of sugar solutions like molasses or fruit, sugar-cane, or sugar-beet juices is carried out with considerable ease, the malt-converted mashies made of starchy raw materials like grains and potatoes must be fermented in batch processes. The optimum pH for the conversion of dextrins, accomplished by malt amylase in the beer during fermentation, is higher than the pH optimum for alcoholic fermentation; this difference will not permit maximum speed for both biochemical processes. Fungal amylase with its lower pH optimum may find application in continuous fermentations.

In a typical continuous process, a portion of the fermenting liquid is withdrawn from the reaction vessel (fermenter) in a continuous flow, and is continuously replaced with the same quantity of fresh wort, thus keeping the concentration of the "three" constant. Continuous processes conveniently are classified into one-tub, two-tub, and multitub systems. In the one-tub system, which is rarely used, the concentrations of the organisms and the product are constantly kept at a maximum, while the concentration of the available substrate is held at the minimum. In the withdrawn portion, the microbial process is practically completed and is ready for further treatment: distillation, purification, recovery, etc. In the two-tub system, the bulk of microbial action is carried out in the first (large) tub, from which part of the fermenting liquid is continuously withdrawn into a second tub, where the fermentation of the remaining sugars is completed. From the second tub, which is usually smaller than the first, the beer is withdrawn into the beer well in the same proportion as from the main tub. Though the sugar content of the inflowing mash may be as high as 15%.

the unfermented-sugar content in the main tub may be as low as 2–3% and in the second tub, 0.1–0.3%. In the Boulanger process (one of the best-known continuous two-tub systems used in alcohol production), the beer from the main fermenter flows continuously into the first of four or six small fermenting tubs and, after the first tub is filled, flows into the next one, and so on. As the last of the small tubs is filled, the completely fermented beer from the first one is withdrawn into the beer well, ready for distillation. Newly prepared sugar-beet juice or molasses solution is continuously fed into the main fermenter. The empty small tubs are immediately refilled, and the process may be carried out for months without interruption. In the multitub system, three or more tubs are connected in series. Freshly prepared raw material is charged continuously into the first tub, from which the liquid flows to the second tub and from there into the third, and so on. The first tub is inoculated in the beginning, or it is supplied constantly with a small amount of fresh inoculum; in this tub the organism propagates and the beer is constantly in the first stage of the "main fermentation" period; in the following tank or tanks the "main fermentation," and in the last tank the "end fermentation," come to completion. In each tank of a multitank system, the turnover of the liquid is faster than in the two-tub systems. The sugar content in the consecutive tanks gradually decreases, and in the last tank it is a few tenths of 1% or less. The advantage of the multitub arrangement is that the various phases of a batch fermentation, being separated in space from each other, can be controlled separately and according to actual need. In the first fermenter, the propagation can be forced by aeration and agitation; in the next fermenters, where the bulk of sugar is fermented, the most heat is generated, and the excess heat can be removed by means of built-in cooling devices; in the last tank, in which the slow gas development fails to prevent the yeast from settling, agitation can be applied.

In *semicontinuous processes*, the substrate (or its components) is fed according to a definite schedule, either in a constant flow or periodically in small batches. The rate of feed in semicontinuous processes (used in yeast production) often follows a nearly logarithmic curve in order to satisfy the organisms, which tend to multiply in logarithmic proportion with the progress of time.

Among the numerous processes that by their nature are *intermediates between batch and continuous systems*, the oldest is the cut system. One-half the fermenting beer from the first tub of a series is transferred into the second one, and both tanks are filled with freshly prepared mash. Then, one-half the contents of the second tube is transferred into the third tub, and both the second and third tubs are filled with fresh mash. The first tub is allowed to complete the fermentation, while the cutting of the actively fermenting beer between two tanks and their refilling goes on in cycle. Usually, each tank is cut 8 hours after being refilled the first time and is ready to be distilled 16–24 hours after the second refill. Including charging, discharging, and cleaning, each fermenter produces a tubful of fermented beer every 32–48 hours (exact time depends upon the concentration of the beer) instead of the 60–72 hours needed in the batch system. In the cut system, the prefermentation period is eliminated, and inoculation is necessary only at the beginning of a season. The production of yeast in most distilleries resembles the cut system.

Other intermediates between the two types are numerous:

(1) In processes like the Boinot method in alcoholic fermentation, or in some citric acid processes, the amount of organisms is nearly constant throughout the process, as is the speed of transformation (dissimilation). The initial and end periods where speed

is slow are very short, and the values of convertible and converted substances follow curves of inverted shape with minimums and maximums typical of batch systems.

(2) The modern compressed-yeast manufacturing methods are semicontinuous. In this 14-hour long process, the concentration of available carbohydrates and nutrient salts is kept nearly constant during the largest part of the typical process, while the final concentration of the yeast is only two to three times its initial value.

(3) In some of the intermediate processes, the values of the "three" fluctuate periodically. During the main fermentation period, the concentration of the organisms and products is reduced from a maximum to a somewhat lower value by the addition of fresh nutrient solutions at regular intervals; it is then allowed to reach the maximum gradually. Fluctuation may occur within one hour to one day. At the same time, the concentration of available raw materials undergoes an inverse fluctuation—that is, from a lower value it is suddenly increased back to the maximum and is then allowed to be reduced gradually to a definite value, from which it is again increased to the maximum.

A combination of these three intermediate types is occasionally practiced.

**Aeration.** In typical aerobic processes (the production of citric acid, acetic acid, penicillin, streptomycin, or yeast), the presence of air (oxygen) is mandatory; in typical anaerobic processes (butanol-acetone fermentation), the absence of air is imperative.

In many processes, the presence of air, especially during the incubation phase when the organism is growing rapidly, is advantageous. Occasionally air is needed only to suppress the anaerobic (fermentative) activity of an organism in order to promote another activity, such as growth. Yeast propagates well both in the presence and in the absence of air, but it ferments sugars more rapidly when air is *absent*; since assimilation is then slower, the larger part of the sugar will be converted into alcohol. In the presence of *excess air*, fermentation is inhibited and assimilation promoted; for this reason nutrient solutions are strongly aerated in modern methods of making compressed yeast and in the propagation of other organisms.

The oxygen of the air, as in aerobic oxidation processes, may take a part in a reaction, as in the oxidation of alcohol to acetic acid, of hexose to gluconic acid, oxalic acid, or citric acid, etc.

Depending upon the specific requirements, air may be supplied in several ways. The most simple is by *surface contact*: the liquid or the moist mass of substrate, preferably in thin layers, is exposed to the atmosphere. Examples are the surface-culture methods in citric acid (see p. 367) or penicillin production (the latter not in use any longer), vinegar production by the Orleans process, retting of flax, and ripening of Roquefort cheese. Infrequently, aeration is accomplished by distributing the liquid (substrate) in the form of a *spray* in the atmosphere in order to offer a large contacting surface area: in some compressed-yeast processes, the inoculated nutrient is constantly withdrawn from the propagating tank and returned to it in the form of a fine spray; in the quick vinegar process, a thin stream of the acid-alcohol-water solution contacts the air as it trickles down through oak shavings.

On a laboratory scale, it is convenient to aerate a large number of flasks containing small amounts of liquid by *shaking* them constantly in a shaking machine. Uniform aeration is thus achieved in each flask. A shaking machine is a convenient device when preparing inocula or carrying out experiments with a large number of small flasks.

The most universally used method of aeration is *bubbling air* through the liquid substrate by a number of devices, the simplest being the open end of an air pipe. Since the surface area of air bubbles and the contact time are the major factors in effective aeration, various devices have been constructed to distribute the air in the form of the smallest possible size of bubbles and to keep the bubbles floating in the liquid as long as possible. The oldest and most generally used of these devices are perforated air tubes. In the most primitive form, this method uses a sparger, which is a perforated ring or spiral tube placed at the bottom of the tank and connected to the air line. In its most elaborate form, the perforated-tube system covers the entire bottom of the vessel, the individual aerating tubes branching diagonally from one or two main lines. A double-tube system contains the distributing tubes in two levels. The holes may be placed at the top, at the bottom, or at both sides of the tubes, facing the bottom at a 45° angle. Aerating tubes are made of tin-coated copper or stainless steel and are constructed so as to be conveniently removable for cleaning.

Smaller bubbles are produced by various types of fine air distributors or fine aerating systems. Distributors of porous ceramic or carbon material are often used in laboratories. Modern industrial practice employs mechanical air distributors, which are of two major types: in one, the air enters the liquid through the tiny holes of a fast-rotating hollow propeller (or other body) into which the air is conducted through the hollow shaft (as in the Vogelbusch method); in the other type, the air is introduced (as relatively large bubbles) into the liquid in the neighborhood of a fast-rotating (1500–3000 r.p.m.) agitator (usually a propeller) which then cuts the air bubbles into extremely small bubbles (as in the de Becze method). Mechanical air distributors, by circulating the liquid, keep the tiny air bubbles floating for a considerable time.

The air requirement of a process is expressed as volume of air per volume of liquid per minute (ml. air/ml. liquid, or cu.ft. air/cu.ft. liquid, per minute). The amount of air needed by a process varies according to the size of the bubbles and the height of the liquid level. Ten to fifty times more air is needed in the form of large bubbles than in the form of finely distributed ones. The proper aeration of a 10-ft.-high liquid requires slightly more than one-half the air needed by a 5-ft.-high liquid of the same volume.

**Temperature Regulation.** The heat generated by the action of microorganisms is considerable; in fermenters not provided with cooling devices, the temperature of the fermenting beer may increase by 20°F. or more. The beer must, therefore, be inoculated well below the optimum temperature, or the increased temperature will promote the production of undesired compounds or will damage the organism itself. Beers in modern fermenters are cooled, most commonly by coils, submerged in the fermenting liquid, through which cold water circulates. Occasionally, the beer is recirculated through heat exchangers outside the fermenters. Smaller tanks, like those in which inoculum is prepared, are cooled by circulating cold water between the double bottoms or in the jacket around the tank side, or by sprinkling cold water to the outer sides of the tank from a perforated ring (part of the downflowing water evaporates, taking considerable heat away from the tank). In processes in which a constant temperature is essential, automatic temperature-control devices keep the temperature within  $\pm 1^\circ$ . Propagating vessels used for making inocula and tanks used for processes requiring fairly constant temperatures (propagations, oxidations, biosyntheses) are provided with elaborate cooling systems.

**Control of pH** (see "Neutralizing agents," p. 339). The most convenient method

for neutralizing the bulk of the acids formed during the process is to add a sufficient amount of precipitated calcium carbonate (see *Calcium compounds*) (usually sterilized separately in the form of aqueous sludge) at the beginning of the fermentation process. With the aid of slight agitation, precipitated calcium carbonate remains suspended in the liquid, whereas ground limestone (a cheap neutralizing agent occasionally added to the medium) would settle to the bottom of the fermenter. In the production of, for example, lactic acid, gluconic acid, butanol-acetone, 2,3-butanediol, penicillin, streptomycin, and citric acid, calcium carbonate is frequently added to the substrate at the start of the fermentation process. In fermenting butanol and lactic mash, lime hydrate slurry is usually added in regulated amounts at special intervals. In the production of compressed yeast, the excess acid, formed from ammonium sulfate, is neutralized by liquid ammonia, added continuously or periodically to the propagating vessel.

**Fermenters.** Regardless of the nature of the process (fermentation, aerobic oxidation, propagation, or biosynthesis), the containers in which deep-culture (submerged) microbial actions are carried out are usually referred to as "fermenters." Fermenters may be made from the 1-gal. experimental size up to and above 100,000-gal. industrial sizes. They may be cubical or cylindrical, and their horizontal and vertical dimensions may equal each other or may be different. They may be used in a horizontal or vertical position. They may be open on the top or entirely closed. Housings for other than submerged microbial processes are called chambers, propagators, builders, etc.

Modern fermenters are closed, upright cylinders with conical or concave bottom, and they are provided with automatic temperature control, agitation, means of aeration (if needed), and devices for automatic cleaning and steam sterilization. They have aseptic connections to the inoculum and nutrient tanks and are provided with safety valves, sample cocks, thermometers, pressure meters (preferably of the recording type), etc. Fermenters are built of wood (cypress), steel, glass-lined steel, stainless steel, tin-coated copper, concrete, and tile.

Many of the submerged pure-culture processes (butanol-acetone, penicillin, deep-culture citric acid, and others) are carried out in closed fermenters under excess pressure of air or of the fermentation gases to prevent contaminants from entering the tanks. When sterility is imperative, connecting pipe lines are made of tin-coated copper or stainless steel, and the valves and unions of brass. These metals conduct heat well, which is essential for steam sterilization, and offer a smooth surface that is easy to clean.

#### TREATMENT OF SUBSTRATE AFTER FERMENTATION—RECOVERY

Completion of fermentation usually is not the last of the processing steps, but is followed by a physical and/or chemical treatment of the substrate to obtain a product of appearance, purity, concentration, final aroma, etc., demanded by the customers' needs or tastes. Such treatments aim at one, or a combination, of three purposes: (1) separation of the metabolic products from the rest of the substrate (residue of raw materials, auxiliary materials, and diluting agent) and the further separation of the various metabolic products from each other; (2) in the case of metabolites, which like lactic acid are formed partly as the free acid and partly as a salt, the conversion of the metabolite into the desired form, either acid or salt; and (3) development of additional characteristics such as taste, aroma, and color by the formation, or addition, of trace

substances to the metabolic product. The most common *physical treatments* are filtration, chilling, heating, distillation, evaporation, crystallization, washing, sedimentation, decanting, agitation, solvent extraction, carbon treatment, and adsorption followed by elution. Precipitation, neutralization, acid liberation, alkaline treatment, oxidation-reduction, and supplementation with taste- and aroma-providing substances are examples of common *chemical treatments*.

The afterfermentation treatment may be as simple as one single step or may be quite elaborate, that is, composed of a long series of combined chemical and physical treatments. **Volatile metabolites** like ethanol, butanol, acetone, the amyl alcohols, esters, and aldehydes are separated from the fermentation residue by distillation in a "beer still"; and the product of this first distillation is fractionated into its components to the desired degree by a second distillation in a fractionating-column system. **Undissolved residues**, precipitates, or cloudiness are eliminated by filtration or, occasionally, by centrifugal sedimentation. Liquids are filtered in frame-and-plate type filters, Seitz filters, rotary filters, and Sparkler filters, using filter paper, filter cloth, and filter cord as a filtering surface. Frequently, a precoat is developed on the filtering surface with asbestos fibers, paper pulp, diatomaceous earth, or gypsum as filter-aid; sometimes, the filter-aid is mixed with the liquid, and the mixture is filtered. High-grade **purification** is obtained by crystallizing or precipitating salts (usually calcium salts) and by crystallizing acids from their mother liquor. Colors are removed by carbon treatment. Impurities are precipitated out by added chemicals. Additional aroma is developed by aging. Minute quantities of biosynthetics are purified by being adsorbed on surface-active agents and eluted after the fermentation residue is washed away. 2,3-Butanediol and biosynthetics are separated from their fermented substrates by filtration and/or concentration by means of selective solvents, which are usually added at a specific pH.

The following examples illustrate the practical application of physical and/or chemical processes in the various afterfermentation treatments. Fermented milk products like buttermilk, kefir, and yoghurt are only cooled. Vinegar is usually filtered and diluted, and sometimes colored and flavored. Beers and wines are filtered and cooled and often aged; beers are also carbonated, and wines are often flavored with spicy herbs or fortified with brandies before marketing. Brandies, whiskies, and rums are distilled from their corresponding fermented mash (wines and beers), usually to a certain proof, and are aged in specific barrels for a predetermined time; after aging they are frequently blended (see *Alcoholic beverages, distilled*). In the production of industrial alcohol, distillation systems, often of considerable complexity, are employed (see *Alcohol, industrial*). Citric acid is precipitated as its calcium salt, from which it is liberated by sulfuric acid (see p. 369). In the production of lactic acid, the fermented mash is neutralized with calcium carbonate or hydroxide, and the solution of calcium lactate is concentrated (see p. 363). Compressed yeast is separated from its exhausted nutrient broth by the use of centrifugal separators (see p. 373).

#### BY-PRODUCTS

The recovery and marketing of by-products—the remainder of the substrate after the desired metabolite is removed, or the remainder of the raw material after the substrate (wort, beer, media) is produced—often adds to the economy of a microbial process. The protein, fat, and mineral content in the residue of starchy raw materials (grains, potatoes) is in fact increased by the removal of the starch during fermentation.

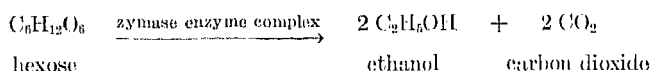


The vitamin content (mainly the B group) and as yet unidentified growth factors remaining in the fermentation residue can often become hundreds of times higher than in the original raw material. Some by-products are even marketed occasionally at a price higher than that of the raw material itself. Since the fermentation residue of grain mashes is approximately one-third the amount of the original raw material, this recovery has developed into an essential agricultural industry: dried brewers' yeast and brewers' dried feed (by-products of beermaking), distillers' dried grains and distillers' solubles (by-products of grain distilleries), and the dried residues of butanol-acetone mashes are of primary interest to the feed-manufacturing industry (see *Alcohol, industrial*; *Beer*; *Feeds, animal*).

### Alcoholic Fermentation

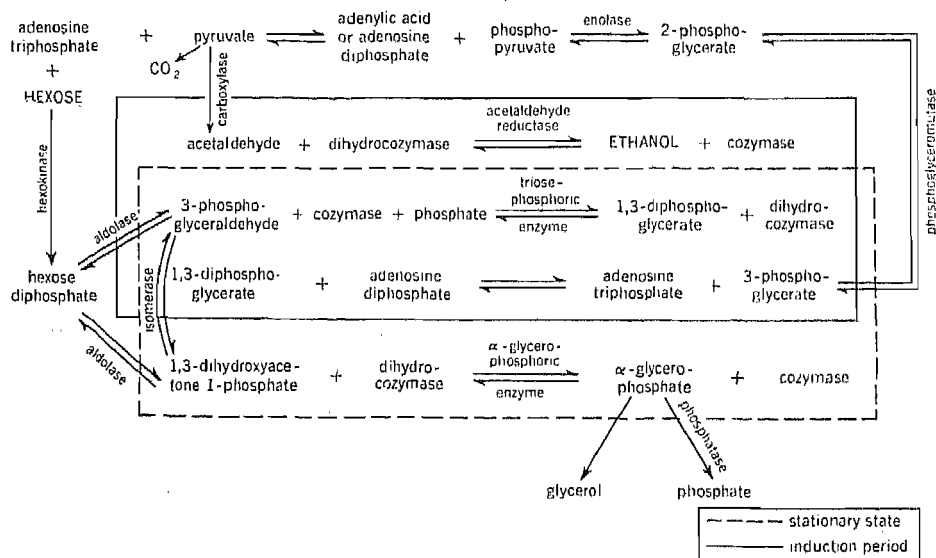
#### MECHANISM

An equation that merely represents the overall process whereby sugar is eventually transformed into ethanol and carbon dioxide is:



Actually, a large number of closely interrelated reactions are involved. These may be divided into oxidation-reduction and phosphorylation steps, as well as certain special reactions. All of these reactions are catalyzed by highly specific enzymes. A scheme of the entire, complex process was shown in Scheme 1, which is based mainly on the pioneering work of Embden and Meyerhof, as well as on contributions made by other investigators.

**Scheme 2. Alcoholic Fermentation (based chiefly on the work of Embden and Meyerhof).**

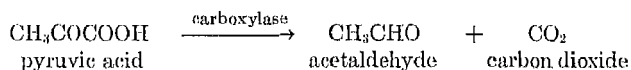


It will be noted (see Scheme 2) that a distinction is made between the *induction period* and the *stationary state* of fermentation. During the former stage, the two triose phosphate compounds (3-phosphoglyceraldehyde and 1,3-dihydroxyacetone 1-

phosphate), produced from hexose diphosphate through the action of the enzyme aldolase, interact in a coenzyme-linked series of reactions to form  $\alpha$ -glycerophosphate ( $\alpha$ -glycerophosphoric acid) and 3-phosphoglycerate (glyceric acid 3-phosphate). The glycerol, produced during this induction period, is liberated from the glycerophosphate by phosphatase action. The phosphoglycerate is transformed through a sequence of consecutive enzymic reactions into pyruvate. As soon as sufficient acetaldehyde becomes available through the decarboxylation of the pyruvate, it takes over the role of hydrogen acceptor from the dihydroxyacetone phosphate, and, by interaction with dihydrocozymase, ethanol is produced. This latter process predominates during the stationary state of fermentation, thereby blocking the formation of glycerol from the dihydroxyacetone phosphate.

If, on the other hand, the acetaldehyde is trapped through the addition of sulfite or bisulfite, or if it is disproportionated into ethanol and acetic acid (Cannizzaro reaction) through shifting the pH to the alkaline region, the induction phase of fermentation is perpetuated, and glycerol continues to be produced in appreciable amounts.

With the exception of the decarboxylation reaction:



all the intermediate steps indicated in Scheme 2 are reversible in nature. There is evidence, from recent work by Calvin with radioactive carbon, that a large part of the same process, but going in the reverse direction, is involved in photosynthesis, where carbon dioxide is transformed into sugar through a series of photochemical and of dark reactions.

Compound carbohydrates, such as starch, are not directly fermented, but they are first split and transformed into free hexose molecules or into hexose phosphate through the action of specific enzyme systems (amylase and phosphorylase, respectively). In the latter instance, the primary product is glucose 1-phosphate (Cori ester). This is then transformed into glucose 6-phosphate (Robison ester) and, successively, into fructose 6-phosphate (Neuberg ester) and, finally, fructose 1,6-diphosphate (Harden-Young ester). Fermentation proper may be considered to start at that point.

It has been demonstrated by Hanes, Kiessling, and Cori that these preparatory reactions are also fully reversible: starch and glycogen have been synthesized by these workers from Cori ester *in vitro* with the aid of specific enzymes isolated from plant and animal tissues. For the synthesis, small amounts of the polysaccharides are required as "primers." They form the nuclei of the synthetic polymer carbohydrates to which additional chain links (hexose molecules) are added through phosphorylase action to form either unbranched or branched chains, depending upon the type of primer carbohydrate employed.

#### SECONDARY PRODUCTS OF ALCOHOLIC FERMENTATION

When 100 grams of hexose is fermented, the amount of ethanol and carbon dioxide totals about 90–95 grams. Besides ethanol, in varying amounts, a number of other compounds are formed during the alcoholic fermentation. They are partly intermediates of the alcoholic fermentation (Schemes 1 and 2), partly metabolic products derived from yeast activity other than alcoholic fermentation, and partly contaminants—that is, compounds formed by organisms other than yeast. All these compounds are commonly referred to as the secondary products. Their proportion is in-

Compound	Weight, g.	Compound	Weight
Acetaldehyde.....	0.01-0.08	Ammonia.....	Trace
Acetic acid.....	0.05-0.50	Ethylamine.....	Trace
2,3-Butanediol.....	0.06-0.10	Propionaldehyde.....	Trace
Glycerol.....	2.5-3.6	Acrolein.....	Trace
Lactic acid.....	0.20-0.40	Isobutyraldehyde.....	Trace
Succinic acid.....	0.50-0.70	<i>tert</i> -Butyl alcohol.....	Trace
Fusel oil.....	0.35-0.70	Formic acid.....	Trace
Methanol.....	0.00-0.10	Butyric acid.....	Trace
Furfural.....	Trace	Esters.....	Trace
Acetone.....	Trace		

activated carbon, oxidation (by potassium permanganate or other substances), or a combination of the three.

#### MICROORGANISMS USED IN ALCOHOLIC FERMENTATIONS

Ethanol is produced by many species of yeasts, bacteria, and molds. Industrial methods generally employ yeasts exclusively as fermenting agents; in making alcohol, whiskey, and beer, acclimated strains of *Saccharomyces cerevisiae* are used almost exclusively; in wine production, special strains of *Saccharomyces ellipsoideus* and *Saccharomyces pastorianus*; in the fermentation of oriental and tropical mashes, several other species of the genera *Saccharomyces* and *Schizosaccharomyces* are utilized.

Occasionally, certain lactic-acid-producing bacteria and amylase-producing molds are used as auxiliary organisms to aid the action of the yeast. Lactic acid serves a dual purpose: it is beneficial to the growth of yeast and also prevents the growth of many undesired organisms. Most frequently, *Lactobacillus delbrueckii* is used to acidify and predigest grain mashes prepared as media for yeast propagation. Amylase-producing molds are used to convert the starch of raw materials into maltose either before or during fermentation. Mold amylase assures higher alcohol yields than malt amylase and is active at a low pH at which malt amylase activity is almost nil. Molded bran has been tested in large plant-scale operations and the application of molded stillage is in progress. The Amylo process (see Vol. 1, p. 259), because of the long fermentation time and low alcohol yield, is considered obsolete by many workers.

**Yeasts (q.v.).** The unification of classification, nomenclature, and characterization of yeasts described during the last six decades is in progress. The Stelling-Dekker system places typical yeasts into two genera: *Saccharomyces* and *Schizosaccharomyces*, and further divides *Saccharomyces* into two subgenera, *Saccharomyces* and *Zygosaccharomyces* (they differ in the mode of germination of the ascospores). It specifies 24 species in the subgenus *Saccharomyces*, 17 in subgenus *Zygosaccharomyces*, and 2 or 3 species in the genus *Schizosaccharomyces*. The few hundred yeasts described under various names are considered in Stelling-Dekker's system as variants or strains of these.

*Saccharomyces cerevisiae* comprises the largest number of yeast strains described and used industrially. Almost all yeasts used in the making of alcohol, beer, wine, brandy, rum, whiskey, and bread are variants or strains of this species. It grows aerobically or anaerobically. In the first case, the bulk of available carbohydrates is assimilated, and the required energy for growth and reproduction is obtained by aerobic respiration. In the second case, the bulk (85% or more) of available carbohydrates is fermented into alcohol and carbon dioxide, a fraction (5-10%) into secondary products, and only a small portion (4-6%) is assimilated. Glucose, fructose, mannose, sucrose, and maltose are easily fermented; galactose is fermented with difficulty; raffinose is fermented completely by bottom yeasts (see below) but only one-third by top yeast; lactose is not fermented.

The cells are generally oval, often round, and occasionally elongated. Infrequently, they form pseudomycelia, but they never form true mycelia. They reproduce by budding, which may occur at any region of the cell. The mother cells of many strains form clusters with their offspring, thus forming the branched budding yeasts, typical of most brewers' yeasts. In elongated cells, budding may occur only at the terminal ends; the cells may part after the daughter cell reaches maturity, or two or four cells may remain in chains. The appearance of budding cells is frequently typical of a variant or a strain. In un aerated liquids, the location of the propagating cells during fermentation is also characteristic of the strain. There are bottom-fermenting yeasts (bottom yeast), top-fermenting yeasts (top yeast), and intermediate forms.

The size of typical cells is approximately  $3-7 \times 4-14$  microns. In old cultures, very elongated cells ( $3-7 \times 50-80$  microns) are frequently seen.

The one to four spores (round-, oval-, kidney-, or hat-shaped) are formed by parthenogenesis (asexually), unlike the cells of the species in subgenus *Zygosaccharomyces*. Spores are usually 2-4 microns in diameter.

Yeasts propagated under almost identical conditions for several decades in the same brewery,

grain, rum, or molasses distillery, or compressed-yeast plant, exhibit permanent characteristics by which they are identified as variants of special strains of *S. cerevisiae*. Many of the variants were described by earlier investigators as individual species, but because of their morphological and biochemical characteristics now are considered as well-defined variants of the same species. The best-known variants (Russen) are compressed-yeast Rasse II, Rasse XII, Delft<sub>a</sub> (Rasse Delft I), Delft<sub>b</sub> (Rasse Delft II); all are used in compressed-yeast production and molasses distilleries. Rasse Froberg, bottom-fermenting yeast, and Rasse Saaz, top-fermenting yeast, are used in breweries and grain distilleries. Rasse Johannisberg I, Rasse Johannisberg II var. *ellipsoides*, and Tokay 22 are utilized in wineries. Rasse Champagne and Rasse Bussy are yeasts used in making champagne. Rasse saké (or, commonly, saké yeast) was isolated from koji in Japan, Rasse batatae (*S. batatae* Saito) from a batata distillery (by Saito), and Rasse ananensis from sugar cane (in Annam by Henri-ri; Rasse ananensis propagates at temperatures as high as 43°C.). *Saccharomyces carlsbergensis* (several variants described), a bottom-fermenting yeast, and *S. logos* (*S. brasiliensis* used in Rio de Janeiro), commonly called Logos yeast, are also used in breweries and distilleries. The best-described species of *Zygosaccharomyces*, also of some industrial interest, are *Z. barkeri*, *Z. bailii*, *Z. japonicus*, *Z. lactis*, *Z. mellis acidii*, *Z. mandshuricus*, *Z. fermentati*, *Z. vini*, and *Z. marxianus*. Yeast belonging to the genus *Schizosaccharomyces* (fission yeasts), like *S. pombe*, *S. octosporus*, and *S. mellacii*, are occasionally used in special processes.

**Bacteria.** *Lactobacillus delbrueckii* grows with great speed at temperatures between 44 and 50°C. in a malt-converted mash. A 1-gal. inoculum in a 1000-gal. mash may reach maximum population within 12–14 hours. At temperatures of 50–55°C., without any special care, the culture remains considerably pure. Possible contamination is suppressed by the temperature, the fast propagation, and the lactic acid and antibiotics formed. These nonmotile, non-sporeforming, thin, long cells (0.5–0.7 × 15–30 microns), often form chains several hundred microns long. They require a number of amino acids and growth factors, which are supplied in sufficient quantities in a malt-converted grain mash. *L. delbrueckii* ferments glucose, fructose, maltose, sucrose, lactose, and dextrins into lactic acid. It is destroyed within 10 minutes at a temperature above 70°C.

A number of other lactic-acid-producing bacteria can play a role in the acidification of spontaneous lactic mashes: *Lactobacillus beijerinckii*, *L. fermenti*, *L. hayduckii* (*L. buchneri*), *L. hyschi*, *L. leichmannii*, *L. maercki*, *L. plantarum*, etc.

*Lactococcus agglutinans* and other species may cause the clumping of yeast cells in a fermenting beer.

Among the many bacteria capable of producing ethanol from carbohydrates are: *Bacillus acetoethylicum*, *Pseudomonas lindneri* (*Termobacterium mobile*), and *Sarcina ventriculi*, known to produce chiefly ethanol when fermenting glucose. *Bacillus acetoethylicum* and *B. macerans* produce ethanol in addition to acetone, as does *Clostridium acetobutylicum* (in addition to acetone and butanol). *Bacillus polymyxa* produces considerable amounts of ethanol in addition to 2,3-butanediol.

**Molds.** The molds used in the Amylo process are commonly referred to as "amylomyces" (plural "amylomycetes"). The best known are the following: *Mucor rouxianus*, also called "amylomyces α," isolated from Chinese yeast, converts and ferments starch but will not ferment sucrose. *Rhizopus japonicus*, also called "amylomyces β," isolated from Japanese koji, grows best at 36–37°C. It ferments sucrose, raffinose, inulin, and melibiose, with the production of a maximum of 5% ethanol in the mash. *R. tonkinensis*, also called "amylomyces γ," does not ferment sucrose, raffinose, inulin, or melibiose. *R. delemar* and *Mucor boudard*, also of Oriental origin, are occasionally used in the Amylo process.

*Aspergillus oryzae*, *A. flavus*, and *A. niger* are amylase-producing molds having

future prospects in ethanol production. Many molds, especially when grown under submerged conditions, produce ethanol. *Mucor erectus* produces 8%, *M. racemosus* 7%, *M. stolonifer* 3%, and *Rhizopus delemar* 2–3% (by volume), but their fermentation speed is low. Several species of *Mucor*, under submerged conditions, develop special cells that reproduce by budding, in a manner similar to yeasts. Under the microscope, these budding cells are occasionally difficult to distinguish from regular yeasts. They change to the mycelium stage when grown on the surface of a nutrient medium.

#### EFFECT OF YEASTS ON CARBOHYDRATES

Various yeasts differ in their ability to utilize the various carbohydrates. Some yeasts grow on many kinds of carbohydrates; most yeasts exhibit a preference for certain sugars; and still others use only one kind. Some yeasts utilize only monosaccharides while others prefer polysaccharides. The three-, six-, and nine-carbon sugars, and hexose polymers answering to the general formula  $(C_6H_{10}O_5)_n$ , are fermented by yeasts, but tetroses, pentoses, or heptoses are not. All raw materials used for alcoholic fermentation by the industry contain hexoses or compounds which yield hexoses on hydrolysis.

Among the naturally occurring hexoses, D-glucose, D-fructose, and D-mannose are easily fermented. Glucose is fermented by almost every yeast and at a faster rate than the other sugars. Galactose generally is fermented slowly, or not at all, by many yeasts. The relative positions of the hydrogen atoms and the hydroxyl groups appear to govern the ease of fermentation: on the third, fourth, and fifth carbons in the glucose, fructose, and mannose molecules, the positions of the hydrogen atoms and hydroxyl groups are identical.

Polysaccharides are usually fermented indirectly, that is, they are first hydrolyzed to monosaccharides. Thus yeast lacking a particular hydrolytic enzyme will not ferment the corresponding sugar, as shown by the inability of *Saccharomyces cerevisiae* to ferment lactose. Hydrolysis may be well ahead of fermentation; all the sucrose in a liquid, for example, may be inverted before one-half of it is fermented. On the other hand, the speed of fermentation is often checked by slow hydrolyzing activity.

It is believed that some disaccharides, at least in part, are fermented directly, without previous hydrolysis. In such cases, the fermentation speed is higher than that which follows hydrolysis. Some yeasts ferment the disaccharide lactose faster than either of its monosaccharide components, glucose or galactose, or their mixture. Lactose is often fermented at such a high acidity (pH 3) that the activity of the lactase is completely suppressed.

Regardless of the mechanism of the cleavage, the ability to ferment one or several particular disaccharides is fairly specific to a yeast.

Among the disaccharides are:

(1)  $C_4$ -linked sugars: maltose, 4-( $\alpha$ -glucosyl)glucose; cellobiose, 4-( $\beta$ -glucosyl)-glucose; lactose, 4-( $\beta$ -galactosyl)glucose. (2)  $C_6$ -linked sugars: melibiose, 6-( $\alpha$ -galactosyl)glucose; gentiobiose, 6-( $\beta$ -glucosyl)glucose; turanose, 3-( $\alpha$ -glucosyl)fructose. All are reducing disaccharides having one free reducing group in the molecule. Sucrose, an  $\alpha$ -glucopyranosyl  $\beta$ -fructofuranoside, and trehalose, an  $\alpha$ -glucopyranosyl  $\alpha$ -glucopyranoside, are nonreducing sugars bearing both reducing groups tied into the molecule.

Yeasts can hydrolyze the same type of linkage in glucosides and trisaccharides as in disaccharides; they then ferment the liberated hexose portion. The nonreducing

trisaccharide raffinose, 6-( $\alpha$ -galactosyl)- $\alpha$ -glucosyl  $\beta$ -fructofuranoside, is partially hydrolyzed by yeasts containing either the enzyme sucrase or the enzyme melibiase; one-third of raffinose, the liberated hexose portion, is fermented by the yeast. Complete hydrolysis and fermentation of raffinose are effected by the bottom-fermenting beer yeasts, which contain the two disaccharidases, sucrase and melibiase. The fermentation of rhamninose, robinose, and mannatriose (reducing trisaccharides), gentianose, melezitose, and raffinose (nonreducing trisaccharides), and "stachyose" (nonreducing tetrasaccharide) is of little importance in industrial fermentations.

Industrial mashes that contain *monosaccharides* (almost exclusively glucose, or fructose, or both) are fermented with ease. The maltose of malt-converted starchy mashes also ferments with considerable speed. Common yeasts, being rich in the enzyme maltase, hydrolyze faster than they ferment, and the mash contains more glucose than maltose as the fermentation progresses. The cause of the relatively long "end fermentation period" is the slow conversion of the dextrins at the fermentation pH and temperature of the beers. Both are below the optimum for the action of malt diastase.

Molasses mashes and beet-sugar and sugar-cane juices contain chiefly the *disaccharide* sucrose, besides some invert sugar and raffinose. It is customary to hydrolyze the compound sugars of such mashes before inoculation by boiling them with mineral acids (sulfuric acid). Prehydrolyzed mashes ferment faster and result in higher yields. To save the active diastase enzyme, the malt-converted mashes are not hydrolyzed with mineral acids.

The *polysaccharides*—starch, inulin, and glycogen—are first hydrolyzed and then fermented by yeasts. Starch, composed of 100–2000 glucose units, when partially hydrolyzed by diastase, yields maltose and dextrins; when completely hydrolyzed with mineral acids, it yields glucose. Starch is fermented by a few yeasts only; *Schizosaccharomyces pombe* and *S. octosporus*, for example, hydrolyze and ferment it slowly. Glycogen, stored as a reserve food in well-fed yeast cells, may be fermented to secure energy when yeast is starved. Inulin, present in the Jerusalem artichoke and composed of about 30 fructose units, is hydrolyzed to fructose by the enzyme inulase, and is both hydrolyzed and fermented by several yeasts like *Saccharomyces fragilis*.

#### INDUSTRIAL PROCESSES EMPLOYING ALCOHOLIC FERMENTATION

The kind and sequence of the individual steps of specific processes are described in *Alcohol, industrial*; *Alcoholic beverages, distilled*; *Beer and brewing*; *Wines*. A few characteristics of particular fermentations used in individual industries are given here in brief.

Molasses mashes and sugar-cane and beet-sugar juices are fermented 36–48 hours in batch systems and 18–24 hours in continuous systems. After fermentation is completed, they may contain 8–12% ethanol by volume. Cane-sugar molasses mash in rum production is fermented for 3–5 days and, after completion, contains 5–6% ethanol. The fermentation temperature of these mashes is 28–30°C., and the maximum yeast population during main fermentation is 120–150 million cells per milliliter. 100 gal. of molasses with 50% sugar (sucrose) content yields 80 proof gallons purified alcohol and with 60% sugar (sucrose) content yields 96 proof gallons. (One proof gallon equals one gallon of 50% alcohol by volume at 60°F.)

Sulfite liquor, where available as a waste, is frequently utilized in the manufacture of industrial alcohol alone or in combination with molasses. Before inoculation with

yeast, the sulfite liquor is neutralized with lime, the formed precipitate is eliminated, and the clarified liquid is supplemented with yeast nutrients. Using specially acclimated strains of *Saccharomyces cerevisiae*, the batch fermentation takes 72–96 hours. Continuous fermentation of sulfite liquors is much speedier; a 100-gal. fermenter space yields 100 gal. fermented beer every 24 hours. The resulting liquid contains about 1% alcohol.

Malt-converted grain and potato mashes in whiskey and alcohol production are fermented for 66–96 hours at 28–30°C. and contain 6–8% ethanol by volume when fermentation is completed, while grain mashes for special whiskey production are fermented for 4 days and contain 4–6% ethanol by volume. The maximum yeast population in the beer is 80–150 million cells per milliliter.

Beer is fermented at 8°C. for 8–14 days and has a final ethanol content of 3–8%. Fermentation of fruit mashes (plum, apricot, apple) in making brandies usually is spontaneous, may take 6–12 days depending upon the original sugar content, and may end with 5–12% ethanol by volume.

In wine making, the spontaneous fermentation of grape juices shows three distinct phases: an incubation period, a main fermentation period, and an end fermentation period. With the slow development of carbon dioxide, the incubation or pre-fermentation period may proceed for 1–3 days; the main fermentation period, with vehement gas production, when the bulk of the sugar is fermented, may be completed in 3–6 days; and the end fermentation period, when the gas production is very slow or occasionally ceases for a shorter or longer time, may take from 2 months to 2 years. The maximum yeast population is 150–200 million cells per milliliter. In the finished wine, the ethanol content is 10–21% by volume, depending upon the original sugar content. When the ethanol content reaches 13–15% by volume, the fermentation of the sugar becomes very slow and is performed by the offspring of yeast cells acclimated to the conditions existing in the fermenting vessel (barrel). While modern wineries employ carefully propagated pure-yeast cultures as inoculum (the fermentation is performed by one strain), in spontaneous wine fermentation a number of organisms take part: other organisms (*Botrytis cinerea*, *Sachsis suaveolens*, *Dematium pullulans*, *Saccharomyces apiculatus*, and the non-sporeforming *Torulopsis* species) begin to propagate along with the true wine yeasts. When the ethanol content reaches 4–5%, the typical wine yeast dominates the fermentation of the grape juice.

Raising dough by bakers' yeast or by leaven in breadmaking is primarily the result of alcoholic fermentation. The yeast, metabolizing the sugar, ferments in the dough and even propagates if sufficient time is available. The carbon dioxide and the alcohol vapors formed by the yeast then "raise" the dough (see *Bakery processes*).

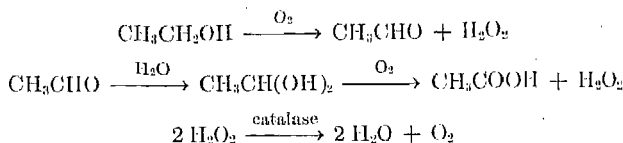
## Acetic Acid Production

### MECHANISM

The oxidation of ethanol to acetic acid (known as the acetification process) by various species of *Acetobacter* is carried out in two steps: (1) dehydrogenation of ethanol to acetaldehyde and (2) dehydrogenation of acetaldehyde hydrate (1,1-ethanediol) to acetic acid. Although, experimentally, quinone, methylene blue, or even acetaldehyde may accept the hydrogen, in natural and in industrial vinegar production oxygen of the air acts as the hydrogen acceptor. See *Acetic acid*; *Vinegar*.



*Aerobic mechanism:*



*Anaerobic reaction (by disproportionation):*



Solutions containing 6–12% ethanol and nutrients (like fruit wines, malt and grain beers, and diluted spirits enriched with nutrients) are spontaneously converted into vinegar when exposed to air. More satisfactory acetification is obtained, however, by controlled methods, in which small portions of the alcoholic solution are added periodically or continuously to a vessel containing vinegar and the appropriate organisms. The liquid abundantly contacts air in the vessel, and part of it is withdrawn in the same proportion as the raw material is added.

In the older, slow, so-called *Orleans* process used in home vinegar production, contact with air occurs on the liquid surface, and the organism (*Acetobacter*) forms either a jellylike compact culture, called *zoogloea*, inside the liquid or a pellicle on the surface. In the *quick process* used industrially, the liquid containing acetic acid and ethanol is trickled through a large-surfaced material (beechwood shavings, charcoal, or ceramic bodies), while air passes through a perforated false bottom of the tank across the contacting material. The *Acetobacter* cells adhere to the surface of the contacting material. In such setups—called *generators*—the liquid is recirculated and frequently cooled to keep the temperature at 26–32°C. Often two or three generators are connected in a series. The alcoholic solution enriched with nutrients is fed to the first generator, and the finished product (vinegar) is drawn from the last generator of the series. In proper operation, 120–126 grams of acetic acid is formed for each 100 grams of ethanol. The automatically controlled Frings generators are the most efficient.

#### ORGANISMS

A good culture is expected to stick well to the contact material, to tolerate high concentrations of the acid, and to convert ethanol quickly and completely to acetic acid without producing unpleasant impurities, especially aldehydes.

*Acetobacter*, non-sporeforming, frequently motile, and generally short rods, occur singly or in chains. Its species can be divided into two groups:

(1) Those able to oxidize acetic acid to carbon dioxide and water (many aerobic fungi in the presence of air also readily oxidize the acetic acid formed into water and carbon dioxide): *A. aceti*, is a motile rod, 0.4–0.8 × 1.0–2.0 microns, which can utilize ammonium salts as the sole source of nitrogen; it has an optimum temperature of 30°C. and is found in vinegar and on souring fruits. *A. xylinum* occurs singly or in chains, is covered with a slimy envelope, and forms a leatherlike, thick *zoogloea*. It is about 2 microns long, has an optimum temperature of 28°C., and is found in vinegar. *A. rancens* is found on wood shavings of the quick-vinegar generators, while *A. pasteurianum* and *A. kuetzingianum* are inhabitants of vinegar made from beer.

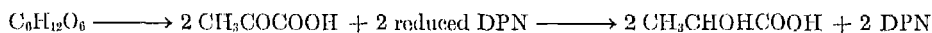
(2) Those that do not oxidize acetic acid: *Acetobacter melanogenum*, *A. roseum*, *A. suboxydans*, and *A. oxydans*, found in beer vinegar and on souring fruits.

Other vinegar producers (such as *Acetobacter acetosum*, *A. ascendens*, *A. aceti-genum*, *A. industrium*, *Bacterium schuezenbachii*, *B. xylinoides*, *B. orleanense*, *B. vini acetati*, and *B. curvum*) described in the literature are species that need closer comparative studies before they can be properly classified.

## Lactic Acid Fermentation

### MECHANISM

Homofermentative lactic acid bacteria hydrolyze compound sugars and dextrins (but not starch) to sugars (hexoses), from which they produce mainly lactic acid (*q.v.*). As in alcoholic fermentation, after phosphorylating the hexose, the organism splits it into two molecules of triose phosphate and converts this into pyruvic acid with the formation of reduced DPN. Pyruvic acid is then reduced to lactic acid:



Another known mechanism for the formation of lactic acid is via the splitting of hexoses into two molecules of methylglyoxal hydrate, which is then converted into lactic acid.

Heterofermentative organisms produce ethanol, acetic acid, carbon dioxide, glycerol, and other compounds, in addition to lactic acid.

Lactic acid is produced industrially by fermenting (malt-converted) corn, whey, molasses, or raw-sugar mashes supplemented with calcium carbonate and inoculated with 0.5–2.5% of an actively fermenting culture of the appropriate organism, usually *Lactobacillus delbrueckii*, *L. leichmannii*, *L. bulgaricus*, or their mixture. In open or closed fermenters made of wood or steel, the fermentation of mashes containing about 10–12% sugar at temperatures of 42–50°C. is usually completed in 3–4 days. During fermentation, the bulk of free acids is continuously neutralized by the calcium carbonate added initially to the mash, or by a calcium hydroxide slurry added periodically to the fermenters. Frequent agitation of the fermenting mash prevents settling of the carbonate. Practical yields are 90–95% of the theoretical.

Lactic acid is recovered from the fermented mash in a long series of steps of physical and chemical treatments: First, the solid grain residue is removed from the fermented liquid by screening. After the screening, a calcium sulfate precipitate is formed by the addition of sulfuric acid and lime; lime also coagulates the fine suspended solids and precipitates some proteinaceous substances. The clear calcium lactate solution containing soluble substances from the grain is obtained by filtering the sluggish substrate through filter presses; the clear liquid is concentrated; and the calcium lactate is crystallized from the concentrate by cooling. The lactic acid is liberated from the filtered and washed crystals by the addition of sulfuric acid, and the lactic acid solution is separated from the calcium sulfate crystals by filtration. Traces of iron are removed by precipitation with potassium ferricyanide, and color impurities are eliminated by carbon treatment. These processes are followed by an additional filtration and a final concentration *in vacuo*.

### ORGANISMS

Among the homofermentative lactic acid bacteria used industrially, the best known are: *Lactobacillus delbrueckii*, *L. bulgaricus*, *L. leichmannii*, and *Bacillus dextralacticus*. Among the heterofermentative forms, the most common are *Lactobacillus brevis* (active in sauerkraut process), *L. buchneri*, *Leuconostoc dextranicum*, and *Strepto-*

*coccus lactis*. Besides these, a large number of other bacteria (*Escherichia coli*, *Aerobacter aerogenes*, and others), molds, and yeasts produce lactic acid in addition to other metabolites.

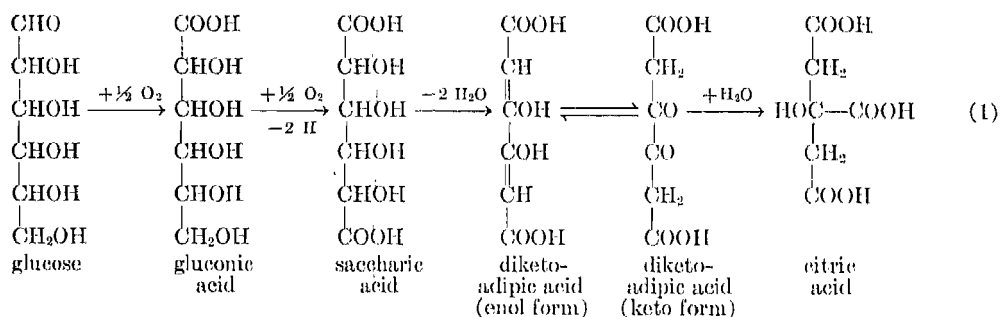
*Lactobacillus delbrueckii* (Leichmann) Beijerinck, known also as *Bacillus acidificans longissimus* Lafar, *Bacillus acidificans* Migula, *Thermobacterium cereale* Orla-Jensen, etc., has been described on page 358.

*Lactobacillus leichmannii* Bergy *et al.*, a nonmotile, non-sporeforming, Gram-positive rod,  $0.6 \times 2.0$ – $4.0$  microns, forms lactic acid from glucose, fructose, maltose, sucrose, and trehalose, but not from lactose, raffinose, arabinose, rhamnose, dextrin, inulin, or starch. This microaerophilic organism produces 1.3–1.5% free lactic acid at temperatures of  $42$ – $44^\circ\text{C}$ ., and in the presence of calcium carbonate is able to convert 10% sugar solutions into calcium lactate. Alone, or mixed with *L. delbrueckii*, it is frequently employed to acidify malt-converted grain mashes in the making of distillers' yeast or in the production of lactic acid. *Lactobacillus bulgaricus* (Leurssen and Kühn), also known as *Bacillus bulgaricus* Leurssen and Kühn, *Thermobacterium bulgaricum* Orla-Jensen, etc., is a non-sporeforming, nonmotile, Gram-positive slender rod found as a natural inhabitant of milk. It successfully ferments lactose, among other sugars, with the production of lactic acid. Optimum temperature for growth and fermentation is  $45$ – $50^\circ\text{C}$ . It is employed in making soured milk products and the manufacture of lactic acid from whey.

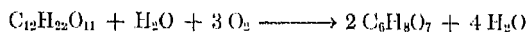
### Citric Acid Production

#### MECHANISM

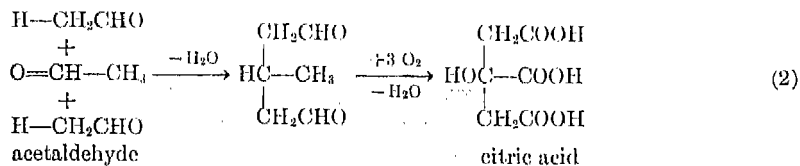
According to one of the two major theories, hexose is oxidized through gluconic acid and saccharic acid to  $\beta,\gamma$ -diketoadipic acid (ketipic acid), and the benzilic acid transformation of the diketoadipic acid then yields citric acid (*q.v.*) (see eq. 1). Theo-

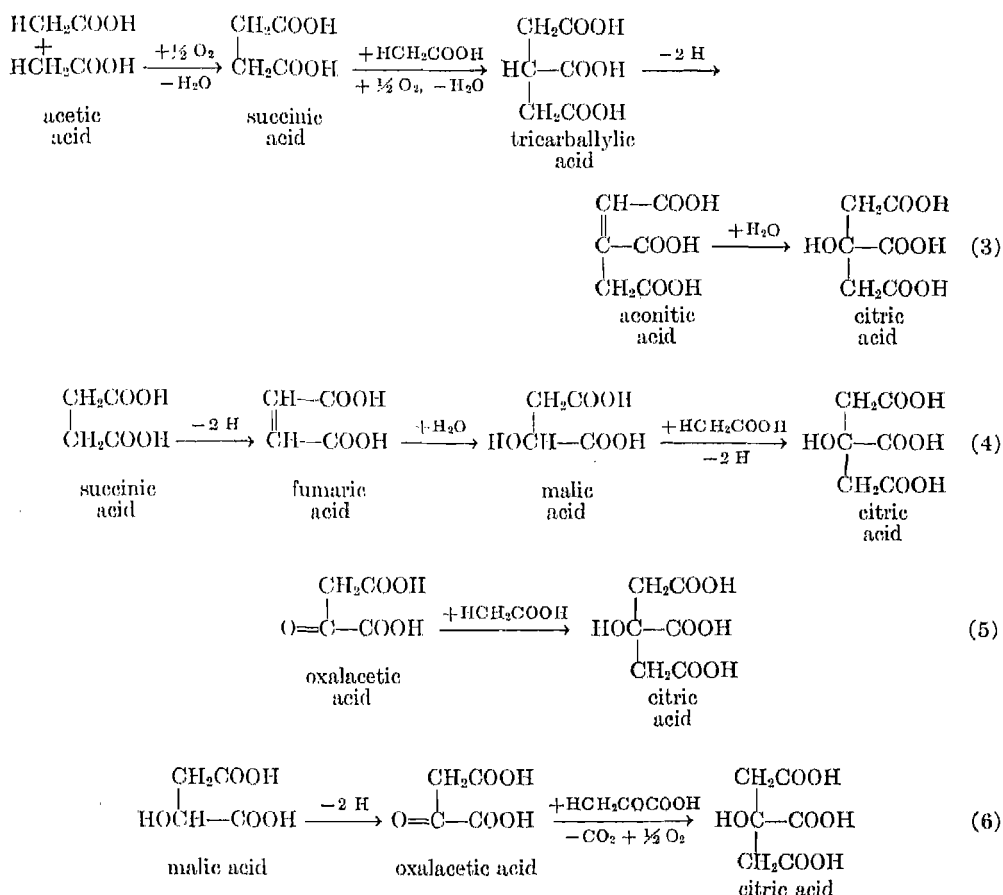


retically one molecule of sucrose yields two molecules of citric acid (1 gram sucrose  $\rightarrow$  1.12 grams citric acid):



According to a second theory, hexose is broken down into smaller molecules, as in alcoholic fermentation, and these smaller compounds then are condensed into citric acid. Equations (2–6) have been suggested to explain this synthesis.





## ORGANISMS

Citric acid, an intermediate metabolic product of the energy-producing oxidative dissimilation of sugars (and also other compounds), is manufactured by a large number of organisms and is assimilated or further dissimilated (usually oxidized to carbon dioxide and water) by many more. Most citric acid producers (outstanding among which are molds), unless environmental conditions are inhibitive, also readily metabolize their product. Among the best known are *Citromyces pfefferianus*, *C. glaber*, *C. citrius*, *Aspergillus niger*, *A. carbonarius*, *A. glaucus*, *A. clavatus*, *A. cinnamomens*, *A. fumarius*, *A. awamori*, *A. aureus*, *Penicillium arenarium*, *P. olivaceum*, *P. divaricatum* (*Paccilomyces varioti*), *P. sangifluus*, *P. glaucum*, *P. luteum*, *P. citrinum*, *Mucor piriformis*, and *Ustilina vulgaris*.

*Citromyces* (now classified as *Penicillium*) is found frequently on lemons. Following Wehmer's recommendation in 1893, species of this mold were first used in industrial production. Grown in a mat on the surface of sugar solutions, *Citromyces* species are able to produce free citric acid up to 8%. Higher concentrations of the calcium salts are obtained when calcium carbonate is added to the medium. At present, *Citromyces* is not utilized by industry because of the low yields obtained and the tendency of this mold to cause further oxidization of the acids produced.

Today, exclusively, special strains of *Aspergillus niger* (first recommended by

Currie in 1917) are employed industrially. Under specific conditions (extreme low pH) they convert sucrose solutions with good yields.

#### MANUFACTURING METHODS

Besides those listed in Table V, Webmer, Bernhauer, Gerhardt, Herrick, Iglaue, Johnson, Moyer, Shu, Thom, Wells, and others contributed valuable research work and helped develop the existing processes. About 17 million pounds of citric acid is produced annually in the U.S. by the microbial process; this is about two-thirds of the total world production. Belgium, Czechoslovakia, France, Germany, Great Britain, Japan, and Russia are also producing citric acid by microbial methods. Details of the actual production methods are not revealed, but, from the material published by investigators and available in patent descriptions, the processing steps and the specific conditions can be reconstructed. The major characteristics of the various processes recommended or used involve specification of the carbon source, inorganic salts, organism, culture methods, pH, surface area of mycelial mat, air supply, temperature, time of conversion (fermentation time), and method of recovery. All manufacturing methods consist of: (1) selecting and preparing the substrate, (2) selecting the organism and preparing the inoculum, (3) microbial action (conversion of sugar to citric acid), and (4) recovery of the citric acid.

**Selecting and Preparing the Substrate.** Citric acid is formed from many *organic compounds* containing 2, 3, 4, 5, 6, 7, 9, and 12 carbon atoms: acetaldehyde, acetic acid, pyruvic acid, glycerol, erythritol, mannitol, arabinose, xylose, mannose, galactose, D-fructose, D-glucose, maltose, sucrose, etc. Technically pure sucrose (cane or beet sugar) is almost exclusively the industrial raw material. Glucose (cerelease) and purified molasses are occasionally used. Malt-converted starch mashes have not proved suitable. Partial hydrolysis of the sucrose or its partial substitution by glucose or fructose decreases the yield. Sugars are diluted to 10–20%.

All elements besides the carbon, hydrogen, and oxygen necessary for the metabolic activities of the mold are supplied in the form of *inorganic salts*. Small quantities of nitrogen, phosphorus, sulfur, magnesium, and potassium, and traces of manganese, iron, and zinc are considered essential. The success of the conversion depends partly on the type and concentration of the salts used and partly on their proportion. Among the various methods, one of the basic differences lies in the specification of the quality and quantity of salts. Salts are added in quantities necessary to promote a subnormal growth: in general, thin mold mats with light or no sporulation produce the best yields; since heavy mycelial growth and sporulation suppress acid production, their development is inhibited by insufficient nutrients. An increase in the amount of salts increases oxalic acid production (above 2%) and reduces the citric acid yield; the aim is to keep the oxalic acid content at less than 10% of the citric acid produced. Ammonium nitrate in concentrations above 2.5 grams per liter favors the formation of a heavy mold mat; more than 0.30 gram of magnesium sulfate promotes sporulation. Ammonium nitrate may be completely replaced by 0.35 gram of potassium nitrate. There is a controversy about the effect of iron and zinc salts: some have found that they increase the yield; others that they increase the mold growth but not the yield; and still others that iron and zinc inhibit citric acid production.

**Preparation of the Raw Material.** This consists simply of dissolving the sugar (120–200 gram/liter) and salt mixture and adjusting the pH. Sterilization of the final solution to avoid hydrolysis and caramelization is usually omitted. The pH of the sugar-salt solution is kept low (1.8–3.5); a pH of 2.00 is preferred. In fact, the utilization of low pH in the medium was the key to the successful utilization of *Aspergillus niger*. At a low pH, oxalic acid formation is retarded, and the solution does not have to be sterilized. An initial low pH is established by the addition of hydrochloric acid. Several variations of both surface and deep-tank methods partially neutralize the citric acid formed—usually by the addition of calcium carbonate. Neutralization is controlled to keep the pH below 3.5. When the initial sugar is higher than 15%, the residual sugar is high in the finished liquor. Table V lists the composition of several recommended media.

**Selection of Organism and Preparation of Inoculum.** Selection of suitable organisms, their

cultivation to obtain a proper inoculum, and the maintenance of their activity are essential for good yields. After the raw material and convenient steps for a processing method are decided upon, a large number of fungi, strains of *Aspergillus niger* and related genera (secured from culture collections, soil, foods, and decaying plant or animal residue), are tested on a laboratory scale for their acid-producing ability before the best strains are applied to commercial production. Even closely related strains are not always similar: some manifest highly variable activities. Various observations and suggestions have been made for maintaining the activity of one or another selected strain: (a) The spores separated from the mycelia of an active strain may be stored in sterile soil, where activity is retained for several years. (b) Spores may be stored at low temperature. (c) Spores should be stored after being desiccated. (d) Stock cultures should be transferred to agar media every 3 or 5 days. (e) The culture, before being used as inoculum for the final broth, should be transferred for several subsequent generations to increasingly concentrated sugar solutions. (f) Activity of some strains may be maintained, while others lose activity when cultivated on solid (malt or must agar) media; lost activity is regained by cultivation of the mold in liquid media in the presence of abundant air. (g) Cultivating or storing the culture at temperatures of 30°C. or above depresses activity. (h) Alternation of liquid and solid media preserves activity. Usually, the pure culture of a strain is used as inoculum or starter. A few recommendations are made, however, for using mixtures of two or three outstanding strains of the same species or for the use of the mixture of *Mucor piriformis* and *Aspergillus niger*. In general, one of five kinds of inocula is used by the various methods: ripe spores harvested from mycelia grown either on solid or liquid media (*A. niger* grows and sporulates abundantly on almost any common laboratory medium); spores germinated in water or liquid media; mycelial pellets raised in submerged liquid media in shaken flasks; a mycelial surface mat grown on a more complete nutrient than the final sugar-salt solution; and a mycelial body raised in agitated and aerated liquid according to the submerged-culture technique. The ripe or germinated spores are the most convenient. Cultures are maintained on sterile media, and inocula are prepared according to the pure-culture technique, but the final sucrose solutions, especially below pH 3.5, need no sterilization.

**Microbial Action.** The development of active mycelia and the suppression of spore formation, infection, side reactions, oxidation of the acid formed, and excess mold growth assure successful conversion. The conversion methods, with regard to the growth of the mold, are of three types: (a) surface-culture, (b) semisolid-culture, and (c) submerged-culture.

The *surface-culture method* is the oldest and the most generally used for commercial production. It was first employed by Wehmer in the *Citromyces* process. The mold mat is grown on the surface of a thin layer (1.5–2.5 in. deep) of sugar-salt broth placed in square (3 × 3 ft. or larger) containers, trays, or shallow pans, usually made of aluminum. For this reason, the process is also called the shallow-pan method. It is estimated that the continuous use of 37,000 pans would be required to yield the citric acid produced in the U.S. A thin liquid layer is required to assure a favorable ratio of surface area to liquid volume during oxidation. The trays are placed a few inches above each other in a closed cabinet provided with facilities for sterilization, ventilation, and temperature control. Sterilization of the equipment before filling it with the broth is necessary. The broth is usually filled from the top plate through overflow tubes. The broth is inoculated with spores or germinated spores, and, after 1 or 2 days, a white sheet of mold mycelia appears on the liquid surface, and the oxidation of the sugar begins. The sugar from the medium enters the cells, and the acid produced from it by the mold cell diffuses back into the liquid medium. When the concentration of the free acids in the medium reaches 7–8%, the oxidation slows down, and it usually stops 7–12 days after the inoculation. The yield obtained from the various raw materials using different strains and methods varies: 70 grams of citric acid from 100 grams of sucrose in a 15% sugar solution is considered normal-to-good in a commercial process; however, on a laboratory scale, yields of 90% or higher are also reported. Each variation of the shallow-pan method described in a patent or a publication claims the elimination of one or another of the existing difficulties. Some of the more important suggestions are: (1) The medium is inoculated by seeding one-fourth to one-half of the liquid surface with the spores separated from the mycelia of a tested active strain. (2) The mold mat is first developed on a rich organic nutrient medium, like sterile dilute barley wort or must, and then the nutrient medium is replaced by sucrose-salt solution. (3) As long as the mold retains its activity, the converted sugar solution underneath the mold mat is replaced every 4 days with fresh sugar solution containing 0.1% potassium nitrate. (4) The mold is raised, and the citric acid production is started in a sugar solution of low concentration; this is later replaced with one of higher concentration. (5) The mold mat at specific intervals is lifted from the surface by means of grates or screens, and the liquid is stirred to eliminate the carbon dioxide. In general, however, it is believed that the mold mat on the liquid surface must

TABLE V. Composition (in Grams) of Sugar-Salt Solutions Recommended by Various Authors for the Production of Citric Acid.

No.	Type of medium	Sucrose <sup>a</sup>	Urea	KNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	KH <sub>2</sub> PO <sub>4</sub>	K <sub>2</sub> HPO <sub>4</sub>	KCl	MgSO <sub>4</sub> ·7H <sub>2</sub> O	MgSO <sub>4</sub> ·4H <sub>2</sub> O	ZnSO <sub>4</sub> ·7H <sub>2</sub> O	Added HCl to pH <sup>b</sup>
1.	Currie, J. N. ....	—	—	—	2-2.5	—	0.75-1.0	—	—	0.20-0.25	—	—	3.4-3.5
2.	Das-Gupta, G. C., <i>et al.</i> ....	—	—	—	2.23	—	—	1.0	—	—	—	—	—
3.	Fulmer, E. I., <i>et al.</i> ....	—	—	3.6	—	—	0.20	—	—	0.10	—	—	—
4.	Chraszcz, T., and Peyros, E. ....	—	—	—	3.0	—	1.0	—	—	1.0	—	—	—
5.	Amelung, H. ....	—	—	—	—	5.0	2.5	—	—	1.2	—	—	—
6.	Wells, P. A., and Herrick, H. T. ....	—	—	—	1.6-3.2	—	0.3-1.0	—	—	0.1-0.5	—	—	—
7.	Baetsle, R. ....	—	—	—	2.0	—	1.0	—	—	0.5	—	—	—
8.	Butkevich, V. S. ....	—	—	—	2.5	—	1.0	—	—	0.2	—	—	—
9.	Butkevich, V. S., and Gaevskaya, M. S. ....	—	—	3.5	—	—	0.3	—	—	0.1	—	—	—
10.	Challenger, F., <i>et al.</i> ....	—	—	—	0.356	—	0.08	—	—	0.08	—	—	—
11.	Chatterjee, N. P. ....	—	—	—	2.2	—	1.0	—	—	0.23	—	—	—
12.	Zaldivar, N. P. ....	—	—	—	2.0	—	3.0	—	—	0.2	—	—	—
13.	Sakaguchi, K. ....	—	—	—	2.0 <sup>c</sup>	—	0.15	—	—	0.10	—	—	—
14.	Bleyer, B. ....	—	—	—	2-2.5	—	0.7-1.0 <sup>d</sup>	—	—	0.2-0.25	—	—	—
15.	Doelger, W. P., and Prescott, S. C. ....	140	—	—	2.25 <sup>e</sup>	—	—	1.0	—	0.25	—	—	1.6-2.2
16.	Szűcs, J.: "growth solution" ....	25-50	—	—	2.25	—	0.3	—	—	0.25	—	—	2.0
17.	Szűcs: "fermentation solution" ....	200	—	—	1.1	—	—	—	0.15	0.25	—	—	1.9
18.	Karow, E. O., and Waksman, S. A.: "growth medium" ....	150	1.0	—	—	—	0.15	—	0.02	0.08	0.02	0.01	2.0
19.	Karow and Waksman: "fermen- tation medium" ....	—	0.5	—	—	—	0.05	—	0.02	—	0.02	0.01	2.0

<sup>a</sup> 125-150 grams if not marked.<sup>b</sup> 2-3.5 if not marked.<sup>c</sup> Also 3 grams of peptone.<sup>d</sup> Calcium phosphate.<sup>e</sup> It can be replaced by 0.35 gram KNO<sub>3</sub>.



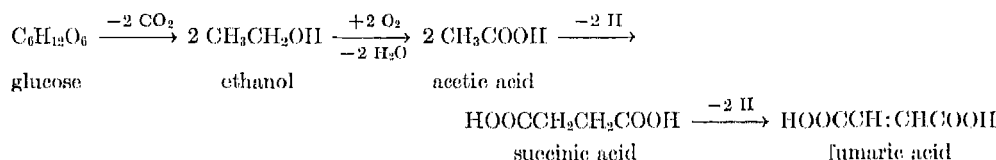


Certain strains of *Aspergillus niger*, *A. fumarius*, *Penicillium purpurogenum* var. *rubrisclerotium*, and *P. chrysogenum* convert glucose almost quantitatively, under controlled conditions, into gluconic acid.

According to the earlier methods, 15–20% glucose solutions containing nutrient minerals when exposed to air in thin layers are oxidized in 8–14 days by a pure culture of the mold grown on the liquid surface. The pH is kept at 3.0–6.4, and the temperature at 25–30°C. The conversion of the glucose is 50–80%. According to the new method, the mold is propagated as a submerged culture in rotary drums in which the substrate is agitated and aerated at a pressure of 30 p.s.i. The sugar is almost completely converted in 1 day or less of processing time. The bulk of the acid formed is neutralized and the optimum pH is maintained by the calcium carbonate initially added to the substrate (about 2.6 grams/100 ml.). Best results are obtained when the substrate is inoculated with the germinated spores of *A. niger* (U.S. Dept. Agr. No. 3 or 67).

### Fumaric Acid Production

Because both ethanol and acetic acid are converted into fumaric acid (see *Malic acid*) by *Rhizopus nigricans*, it is believed that fumaric acid is produced from glucose through ethanol according to the following scheme:



Fumaric acid is produced in small quantities by species of *Rhizopus*, *Mucor*, *Circinella*, *Cunninghamella*, *Penicillium*, and *Aspergillus*. Special strains of *Rhizopus nigricans* may yield 50 grams of fumaric acid from 100 grams of sugar consumed. Glucose, sucrose, molasses, maltose, or starch solutions, supplemented with about 0.4 gram of ammonium salt per 100 grams of carbohydrates, may serve as substrate. Small quantities of magnesium sulfate and dipotassium phosphate ( $\text{K}_2\text{HPO}_4$ ) and traces of zinc or iron salts aid the process. To maintain an optimum pH (approximately 5.0–6.5), the solution is periodically neutralized. Sterile sugar solutions at 28–35°C. are converted by the surface-growth technique in 5–7 days and by the submerged-growth method with agitation and aeration in 24–48 hours.

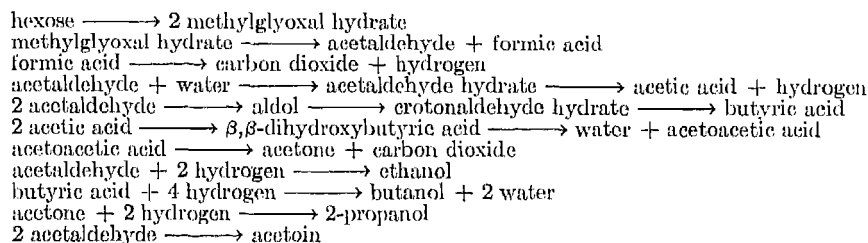
### Ethanol-Acetone Fermentation

*Bacillus macerans*, a motile, sporeforming rod that grows anaerobically or aerobically, ferments pentoses, hexoses, pectin, starch, and glycogen with the formation of acetone, ethanol, organic acids, carbon dioxide, and hydrogen. Mashings containing 8–10% starch at pH 7.6–8.4 and at 39–40°C. are fermented in 3 days. 100 lb. of starch yields about 33 lb. of ethanol, 10 lb. of acetone, and 5 lb. of acids. By this fermentation, known as the Schardinger process, acetone was industrially produced in the earlier part of the century. *B. macerans* is also active in the natural retting of flax and hemp.

## Butanol-Acetone Fermentation

## MECHANISM

Because the proportion of dissimilation products depends upon the culture, substrate composition, and other factors, no single scheme can be expected to explain satisfactorily the fermentation mechanism. Kluyver, Donker, and van der Lak offer the following scheme:



From 100 grams of hexose, approximately the following amounts of metabolic products are formed: acetic acid, 4.7 grams; acetone, 7.2 grams; acetoin (3-hydroxy-2-butanone, acetylmethylcarbinol), 3.1 grams; butanol, 23.0 grams; butyric acid, 2.1 grams; carbon dioxide, 47.5 grams; ethanol, 2.4 grams; hydrogen, 2.08 grams; and traces of formic acid and 2-propanol (isopropyl alcohol). The amounts of components in the distillate obtained from a mash fermented by butanol-acetone producing *Clostridia* are approximately 1 part ethanol, 2-3 parts acetone, and 6-7 parts butanol.

The inoculum is made of the organism grown on potato and on rice media, the two being alternated every second or third day. The activity of the culture is stimulated by holding it in boiling water for 2 minutes before transferring to a fresh medium (see p. 342). 2 liters of a 24-hour culture is sufficient to inoculate 10,000 gal. of mash. The anaerobic condition of the mash, from which the air is blown out during sterilization, is maintained by carrying out the fermentation in closed containers. Depending upon the concentration of the mash and upon the quality of the inoculum, the fermentation is completed in 48-72 hours.

In the mash, during the first 12-15 hours, the increase in carbon dioxide and hydrogen and in the titratable acidity is evidence of the fast growth of the organisms. During the next 10-15 hours, the titratable acidity decreases to about one-half the maximum because of the speedy reduction of the butyric and acetic acids formed. After 30 hours, the fermentation of the remaining carbohydrates proceeds slowly, with a slow increase in solvents (ethanol, butanol, and acetone) and titratable acidity.

## ORGANISMS

In various patents under different names, a number of butanol-acetone producing anaerobes have been described: *Bacillus butylicus* B. F. Ricard., *Bacillus butylacetium* Frieberg, *Clostridium butyricum* (Prazmowski-Pike-Smyth), *Butylobacter zeae* Bakonyi, *Clostridium saccharobutylicum-gamma* Izsak and Funk, and *Clostridium saccharo-acetobutylicum-gamma* Arzberger.

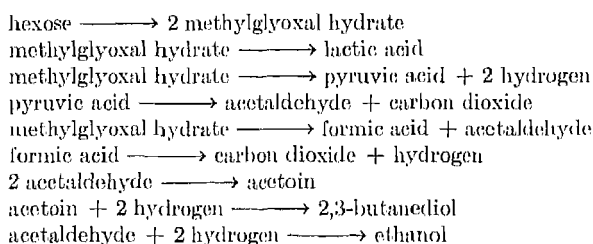
In industrial fermentations, strains of *Clostridium acetobutylicum* McCoy, Fred, Peterson, and Hastings are used to ferment corn, molasses, or sulfite liquor mash. The motile, anaerobic, sporeforming bacilli occur singly or in pairs. The size of vegetative cells is  $0.6\text{--}0.72 \times 2.6\text{--}4.7$  microns; the size of the clostridia is  $1.3\text{--}1.6 \times 4.7\text{--}5.5$  microns. The Gram-positive cells become Gram-negative when aged. Their opti-

imum temperature for growth and fermentation is 37°C. Some strains ferment corn mashes with good yields, and others ferment molasses mashes. The concentration of the solvents in the fermented mash reaches 2.75–3.25% by volume. See also *Acetone*; *Butyl alcohols*.

### Butanediol Fermentation

#### MECHANISM

The formation of 2,3-butanediol (2,3-butylene glycol) (see *Glycols*), ethanol, acetone, carbon dioxide, and hydrogen from sugars by the action of microorganisms may be explained by the following scheme:



During World War II, two processes were developed in the U.S. for the production of 2,3-butanediol. Both were successfully tested in 5,000- to 10,000-gal. pilot-plant fermenters. In one process, malt or acid-converted grain mash enriched with 0.2 gram of ammonium sulfate (or 0.3 gram of urea), 0.15 gram of calcium superphosphate, and 0.3 gram of calcium carbonate per 100 ml., while agitated and aerated, is fermented in 3 days by a pure culture of *Aerobacter aerogenes*. 100 lb. of grain (90% corn and 10% malt) yields 27 lb. butanediol, 4.0 lb. ethanol, and 0.6 lb. acetoin. The highest concentration of solvents (butanediol, ethanol, and acetoin) obtained is 4.65 grams per 100 ml. of finished beer. The optimum for the initial pH is 6.00 and for the fermentation temperature is 30–32°C. In the second process, corn (10–14 grams) cooked with water and supplemented with calcium carbonate (0.3 gram per 100 ml. mash) is fermented by a pure culture of *Bacillus polymyxa* in 2 days. The optimum initial pH is 5.8, and the optimum fermentation temperature is 30–32°C. No aeration is required. From 100 lb. of corn, 15 lb. of butanediol, 10 lb. of ethanol, and 0.6 lb. of acetoin are obtained.

#### ORGANISMS

*Aerobacter aerogenes* (Kruse) Beijerinck, a non-sporeforming, Gram-negative, usually nonmotile rod, 0.5–0.8 × 1.0–2.0 microns, occurs singly or in pairs and is an inhabitant of soil, plants, grains, and the intestinal canal of men and animals. It may utilize citric acid as a sole source of carbon, and urea as a sole source of nitrogen. It grows and ferments best at 30°C. When fermenting carbohydrates, the ratio of gases formed is 1 part of hydrogen to 2 or more parts of carbon dioxide.

*Bacillus polymyxa* (Prazmowski) Migula form fast-moving, sporeforming rods, 0.6–1.0 × 2.5–6.0 microns, which occur singly or in short chains. The spores of this Gram-variant, slime-producing organism are oval, and measure 1.0–1.5 × 1.5–2.5 microns.

### Compressed and Food Yeasts

Since the earliest days of history, the majority of mankind has used leaven for raising dough. (See *Bakery processes; Yeast*). Dormant leaven, a dried portion of a previous batch, contains, besides the unfermented part of the flour, cells of various yeasts, lactic acid bacteria, and molds. When dried leaven is mixed with water, milk, or sugar solutions and then with new flour, the different organisms rapidly begin to propagate and exercise their diversified biochemical activities. Starch is hydrolyzed by molds; lactic acid is formed by the bacteria; ethanol and carbon dioxide are produced by the yeasts; and proteins are partially hydrolyzed by all. Leaven was gradually replaced by washed brewers' yeast. Composed mainly of yeast cells, this yeast raised the bread faster than leaven and greatly aided the large-scale breadmaking of huge city bakeries. The demand created by brewers' yeast led to the development of the compressed-yeast industry.

Modern yeast making developed after the recognition of two basic facts: (1) The yeast, which may propagate both anaerobically and aerobically, assimilates less and ferments more of the available sugars under anaerobic conditions but assimilates in much higher degree and ferments in lesser degree under aerobic conditions. (2) By assimilating inorganic nitrogen, the yeast cell can synthesize proteins and other nitrogen compounds needed for growth, for reproduction, and for the normal functioning of the cells. The first fact led to the aeration of the nutrient wort during propagation, and the second led to the utilization of ammonium salts and liquid ammonia.

Compressed yeast, the common cake yeast used by bakers and housewives, consists of cells of *Saccharomyces cerevisiae* free of foreign substances and almost entirely free from contamination by cells of any other organism. Compressed yeast with special characteristics is made either from grains or from molasses and inorganic salts. Grain yeast which is produced in England, Holland, Denmark, and the U.S., because of its superior qualities and higher cost of production, is priced higher than is molasses yeast and is used only in limited quantities.

From either raw material (grain or molasses), a sterile broth containing 2-4% carbohydrates is first prepared, occasionally supplemented with growth factors. Molasses wort is supplemented with ammonium and phosphate salts (ammonium sulfate and calcium superphosphate or diammonium phosphate). Then the broth is inoculated (pitched) with 0.5-2 grams of yeast per 100 ml. and is aerated and agitated for 12-16 hours. Beginning at about the third hour and continuing until 2-3 hours before the end of the propagation time, fresh, sterile, nutrient broth and salt solutions are introduced continuously into the propagating tank to keep the concentration of nutrients at an optimum level by replacement of the assimilated portion. About 5-8 new cells are developed from each of the pitched cells during the process. Temperature, pH, and titratable acidity are constantly tested and controlled. The broth is kept cooled during propagation, and the excess acids are neutralized by the addition of dilute liquid ammonia. After the broth is exhausted, the cells are separated from the liquid in centrifugal separators, washed with water, and separated from the washing water by centrifugal separators and filter presses. The finished product, the cake yeast, contains 28-31% solids. The protein, ash, phosphate content, and fermenting and proteolytic activity of the cells are predetermined and controlled within certain limitations. The amount of alcohol produced by the yeast during the aerobic propagation is usually too small to pay for the expenses of recovery. However, a few special methods aim at the manufacture of yeast and alcohol in one process. In spite of the many continuous methods available, yeast is generally made according to batch systems. Numerous patents cover the various processing details. To answer special requirements, the pitch yeast in recent years has been prepared from special strains produced by artificial hybridization.

Because of its high nutritional value, yeast is also produced for food and feed purposes, for which high protein (60% or more) and high vitamin content but no enzyme activity are required. Consequently, strains that ferment slowly but assimilate quickly and synthesize vitamins in large quantities

are used for making the seed yeast. Frequently, strains of *Torulopsis utilis* are propagated. The technology is similar to that used for producing bakers' yeast. The nutrient broth is prepared from cheap raw materials like wood sugar, sulfite waste liquors, or molasses. The broth, containing low carbohydrate and high ammonium salt concentrations, is well aerated. For yeasts with a specially high vitamin content, precursors are added to the media: thiazole and pyrimidine compounds added to the wort are readily synthesized to thiamine by the yeast cell. Drying and killing the cells by heat treatment completes the production for food and feed yeast. In some processes, the cells are occasionally hydrolyzed before drying.

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**FERRICYANIDES.** See *Cyanides (ferro-, ferricyanides)*.

**FERRITE.** See *Iron; Steel*.

**FERRO ALLOYS.** See *Iron alloys; Steel*; see also the other element: for example, for ferrochrome see *Chromium and chromium alloys*, Vol. **3**, p. 938; for ferrosilicon see *Silicon*.

**FERROCYANIDES.** See *Cyanides (ferro-, ferricyanides)*.

**FERRUM, Fe.**

Ferrum is the Latin name for iron (*q.v.*) and has been suggested as the international name for this element.

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Fertilizers are materials containing, in available form, one or more nutrient elements essential to plant growth, which are used to supplement the plant-food content of agricultural and horticultural soils.

Extensive use of fertilizers has become established only during the last 100 years. In the Old World the Celts and other European peoples (500 B.C.) were known to have used chalk as a soil amendment. The value of animal manures in stimulating crop plants was known to the ancient Greeks and Romans.

The first use of a fertilizer material other than animal manures was reported in the middle of the 17th century when the German scientist Glauber proposed that saltpeter was the "principal of vegetation," since crops responded vigorously to the application of this material. In England, Sir Kenelm Digby conducted independent experiments during the same period and obtained similar results with saltpeter.

No more important discoveries in the mineral nutrition of plants were published until 1804. At this time the French chemist Théodore de Saussure, who used quantitative analytical methods on the ash of plants, proved that plants contained mineral elements derived from the soil, but placed little emphasis on their essentiality to plant growth. He also believed that plants obtained most of their nitrogen from the soil. De Saussure's work was not accepted as true, but in the 1830's Boussingault verified his findings through field and laboratory experiments at his farm in Alsace. At this, the "first agricultural experiment station," he reintroduced the quantitative methods of de Saussure. He kept close account of the amounts and composition of the fertilizers used and developed a balance sheet showing to what extent the nutrient needs of crops were satisfied from the added fertilizers. Boussingault concluded that legumes alone possessed the power of appropriating as food the nitrogen from the air.

None of these men made the impact upon agricultural theory and practice that did the teachings of von Liebig, who is often called "Father of Agricultural Chemistry." He studied the chemical composition of plants. His results led him in 1840 to propose the mineral theory of plant nutrition in his then-sensational report: "Chemistry in Its Application to Agriculture and Physiology." In 1845, he demonstrated the essential nature of potash and emphasized the need for phosphorus. Liebig's publications led to the commercial preparation of "manures" which in later years developed into the great commercial fertilizer industry.

A few years after Liebig's first work, the team of Sir John Bennet Lawes and Sir Joseph Henry Gilbert established the "second agricultural experiment station" at Rothamsted, the estate of the Lawes family. For over fifty years these men conducted experiments in the use of fertilizers and animal manures in field plots and in the laboratory. To them is attributed the method of treating phosphates from mineral sources with sulfuric acid to form superphosphate, which they turned into a commercial enterprise (7,12).

In 1849 the first mixed fertilizers were made in the United States by P. S. Chappell and William Davison at Baltimore. By 1854, a few hundred tons of mixed fertilizers were being manufactured annually in the U.S., largely in Richmond, Virginia, and Charleston, South Carolina. By 1856, 20,000 tons of mixed fertilizer were manufactured in the U.S., while 60,000 tons of Peruvian and Mexican guanos were imported and consumed.

Table I gives the consumption of fertilizers beginning with the year 1880 according

to the National Fertilizer Association. From 1870 until the outbreak of World War I, the manufacture of fertilizers and its use on American farms developed rapidly. But from 1914 to 1916 consumption dropped 2,000,000 tons and did not reach the 1914 level again until 1920. Then it increased almost without interruption from 1922 to 1930, when it passed the 8,000,000-ton mark. During the economic depression of

TABLE I. Consumption of Fertilizer in the U.S.  
(Thousands of Tons)

Year	Consumption	Year	Consumption	Year	Consumption
1880.....	1,150	1932.....	4,385	1941.....	9,241
1890.....	1,950	1933.....	4,908	1942.....	10,009
1900.....	2,200	1934.....	5,583	1943.....	11,548
1910.....	5,453	1935.....	6,276	1944.....	12,072
1915.....	5,324	1936.....	6,931	1945.....	13,500
1920.....	7,177	1937.....	8,226	1946.....	15,028
1925.....	7,334	1938.....	7,548	1947.....	16,838
1930.....	8,222	1939.....	7,765	1948.....	18,542
1931.....	6,354	1940.....	8,303		

1930-1937, consumption dropped nearly 2,000,000 tons a year for two years and did not reach the 1930 level again until 1937. There was a minor drop in 1938 and 1939, then a rapid rise during and after World War II to a peak of 18,541,885 tons in 1948. The rate of application of nitrogen, phosphoric acid, and potash in various countries according to the National Fertilizer Association is shown in Table II.

TABLE II. Estimated Rate of Fertilizer Application in European Countries, 1949-50.

Country	Rate of application, lb./acre		
	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O
Austria.....	12	18	15
Belgium-Luxemburg.....	86	90	108
Denmark.....	18	25	23
France.....	15	30	22
Western Germany.....	42	50	62
Greece.....	8	11	2
Iceland.....	60	20	20
Eire.....	6	52	7
Italy.....	9	17	3
Netherlands.....	96	106	116
Norway.....	34	34	48
Portugal.....	8	16	2
Sweden.....	11	17	12
Switzerland.....	20	80	38
Turkey.....	4	—	—
United Kingdom.....	27	41	25
U.S.....	6	13	5

### Functions of Plant-Nutrient Elements

All soils contain a number of chemical elements which are necessary for plant growth. It is generally accepted as a fact that plants require the following elements: nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, manganese, copper,



zinc, boron, and, in some cases, molybdenum. All of these are in addition to the elements making up the bulk of the plant tissue, namely, carbon, hydrogen, and oxygen, which plants obtain from the carbon dioxide of the atmosphere and from the soil water. The elements obtained from the soil, also called the mineral elements, though comprising a very small percentage of the plant's total bulk, are essential to the plant's very existence. Without them there is no growth, no photosynthesis, no life.

Nitrogen, phosphorus, and potassium are termed the **major elements** because they are utilized in large quantities by plants and are most likely to be the limiting elements in the soil.

Although the role of the various elements in plant nutrition has been the subject of intensive study, it is still far from thoroughly understood. The notes given below under each element comprise a brief summary of the subject. See also *Plant growth substances*; *Soil chemistry*.

**Nitrogen** comprises 16–18% of the plant protein and other related compounds, and therefore of the protoplasm. Chlorophyll (*q.v.*), the green coloring matter of plants, consists of a complex ring structure in which four nitrogen atoms occupy linkage positions. Lack of nitrogen is readily visible by reduced growth and lack of a healthy green color.

**Phosphorus** is a constituent of various organic compounds in plants such as nucleic acid and phospholipides (phosphatides). A deficiency of phosphorus interferes with the synthesis of these compounds with resulting decreased cell division and seed production. Phosphorus, as phosphates, also acts as the coenzyme of zymase, a system which catalyzes the reaction resulting in ethyl alcohol and carbon dioxide from certain sugars (see *Fermentation*). Root development and early crop maturity are dependent upon phosphorus.

**Potassium** differs from the other two major elements inasmuch as it is not definitely known to be an actual constituent of any of the organic compounds of the plant protoplasm. It is not used in the construction of cell constituents, but it probably plays a regulatory or catalytic role in: (1) translocation of carbohydrates; (2) synthesis of simple sugars, starch, and fibers; (3) reduction of nitrates; (4) synthesis of protein, especially in growing tissues; and (5) cell division. Potassium engenders vigor and disease resistance and is of great importance to such starch- or fiber-producing plants as potatoes, sugar beets, and cotton, and to the legumes, particularly alfalfa.

Calcium, magnesium, and sulfur are known as the **secondary elements**. This is an arbitrary grouping based on the fact that although they are used in considerable quantities by plants, they are not as likely to be as limiting to plant growth on most soils as are the three major elements.

**Calcium** has a wide variety of functions in plant growth. (1) It promotes resistance to disease. (2) It aids neutralization by formation of relatively insoluble compounds of oxalic and other organic acids formed as by-products of cell metabolism. (3) An adequate supply of calcium in the soil is necessary for the thorough inoculation of legumes with their root-nodule bacteria. (4) As the compound calcium pectate, calcium functions as a constituent of cell-wall material. (5) In reducing nitrate nitrogen within the plant, calcium is necessary, although the mechanics of the reaction are unknown. (6) Calcium is a most efficient agent in counteracting an unbalanced supply of other cations to the plant.

**Sulfur** is contained in many plant proteins. The amino acids cystine,  $(\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{S})_2$ , and methionine,  $\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ , contain 26.69% and 21.49% of sulfur, respectively. Sulfur is also a constituent of glutathione,  $\text{C}_6\text{H}_{17}\text{N}_3\text{SO}_6$ , a tripeptide supposed by many investigators to play a part in the respiration process. Chlorophyll development is often retarded in sulfur-deficient plants. The pale green color of such plants soon changes to a deep green when sulfur as sulfate is applied in the root zone or sulfur dioxide is absorbed through leaves. The odors and flavors of such plant species as mustard, onions, and garlic are imparted by sulfur compounds.

**Magnesium** is a constituent of the chlorophyll molecule, of which it comprises 2.7%. Chlorophyll magnesium comprises only a very small fraction of the total leaf magnesium. In order to prevent breakdown of the chlorophyll, the total magnesium content must be several times the quantity present in the chlorophyll. Magnesium acts as a carrier of phosphate and is therefore closely related to the formation of phospholipides and synthesis of nucleoproteins. It is also thought to be required in carbohydrate production and transportation throughout the plant. Magnesium is concentrated

in the reproductive tissues of plants and its relation to seed formation is clear from its importance in fat synthesis (phospholipides).

Copper, manganese, iron, boron, zinc, and molybdenum comprise a group known as the **minor elements or trace elements**. These designations are not altogether satisfactory, since they leave the impression that these elements are not of much importance in plant nutrition. However, the group has been so named because of the very small amounts in which they are found in plants rather than the importance of their functions, because they are fully as necessary as the major or secondary elements. Apparently none of the minor elements enters into permanent protoplasmic compounds within the plant; rather, their effects are those of catalysts, the exact nature of which is not definitely known. There is evidence that the minor elements function as activators of enzymes and plant-growth-regulating substances in the synthesis and utilization within the plant of the many temporary and permanent organic compounds. They may also act directly as catalysts in the synthesis and decomposition of organic compounds. All statements regarding their functions must be accepted as tentative, since proof of the essentiality of these elements is comparatively recent.

**Copper** appears to be an essential component of the oxidizing enzyme catechol oxidase, which is present in potatoes and mushrooms. This is a copper protein compound which contains not less than 0.30% copper. In tung trees, a copper deficiency has resulted in an abnormal accumulation of water-soluble nitrogen in the leaves, while oil synthesis was decreased. In Florida, citrus exanthema, or die-back of shoots, is controlled through copper application. In Australia, oats grown on copper-deficient soils have shown disintegration of the chlorophyll-containing bodies and destruction of the leaf-cell content. Similar results have been obtained on certain Florida soils. Use of copper is recommended on most muck soils, which are particularly deficient in this element.

**Zinc** is a catalyst in oxidation-reduction reactions in plant cells. Auxin, a growth-promoting hormone, may require the presence of zinc to maintain the effective concentration of the hormone. Deficiencies are common in the Southern Coastal Plain, where pecan rosette disease, "white bud" of corn, citrus "mottle leaf," and bronzing of tung leaves are controlled by zinc sprays or soil applications.

**Manganese** acts as a catalyst in conjunction with various oxidizing enzymes, although it apparently takes no actual chemical part in the synthesis. A deficiency of this element usually results in the development of a chlorotic condition in plants. It is also thought to be of importance in the nitrogen metabolism of plants. Manganese deficiencies are common on alkaline soils, on acid sandy soils, which have been limed excessively, and the highly leached sands of Florida citrus areas.

**Iron**, although not entering into the constitution of chlorophyll, is indispensable as a catalyst for its synthesis. Iron is also supposed to act as a catalyst or oxygen carrier in oxidation-reduction processes occurring in living cells. Deficiencies sometimes occur on alkaline soils and are corrected by leaf sprays.

**Boron** is believed to be connected chiefly with protein formation; the element possibly has a catalytic action on the formation of proteins from carbohydrates. However, in common with the other minor elements, more is known about the effects of deficiency than about the actual functions within the plant. In general, a boron deficiency results in stunting, and often the apical buds die back, as is evidenced in alfalfa. A disintegration and decomposition of the tissues in root crops, in the stalks of members of the cabbage family, and "bitter pit" of apple fruits are common symptoms. Requirements of crops vary greatly. Alfalfa, beets, and crucifers require a higher level of boron than do grain crops. Deficiencies are common locally throughout the eastern half of the U.S. and in the Pacific Northwest.

**Molybdenum** was the last of the elements proved essential to plant growth. Known deficiencies in soils are not common and in this country have been confined to small areas in California and New Jersey. Molybdenum improves color and growth of clovers, evidently through a stimulation of the root-nodule nitrogen-fixing bacteria which live in partnership with the legumes. Grasses appear not to be affected by molybdenum deficiency. Molybdenum also seems to stimulate the process of nitrogen fixation by the nonsymbiotic *Azotobacter* bacteria in soils. It is required by tomato plants for survival, although the function in tomatoes is not known at the present time. It has also been shown that lettuce deficient in molybdenum developed chlorosis, failed to form compact hearts, and finally withered.

Four other elements are taken from the soil by plants, but their essentiality has not been proved. In beets and in cotton particularly, **sodium** has given growth responses, especially where potassium is deficient. The beneficial effect of sodium on plants usually decreases as the potassium level increases.

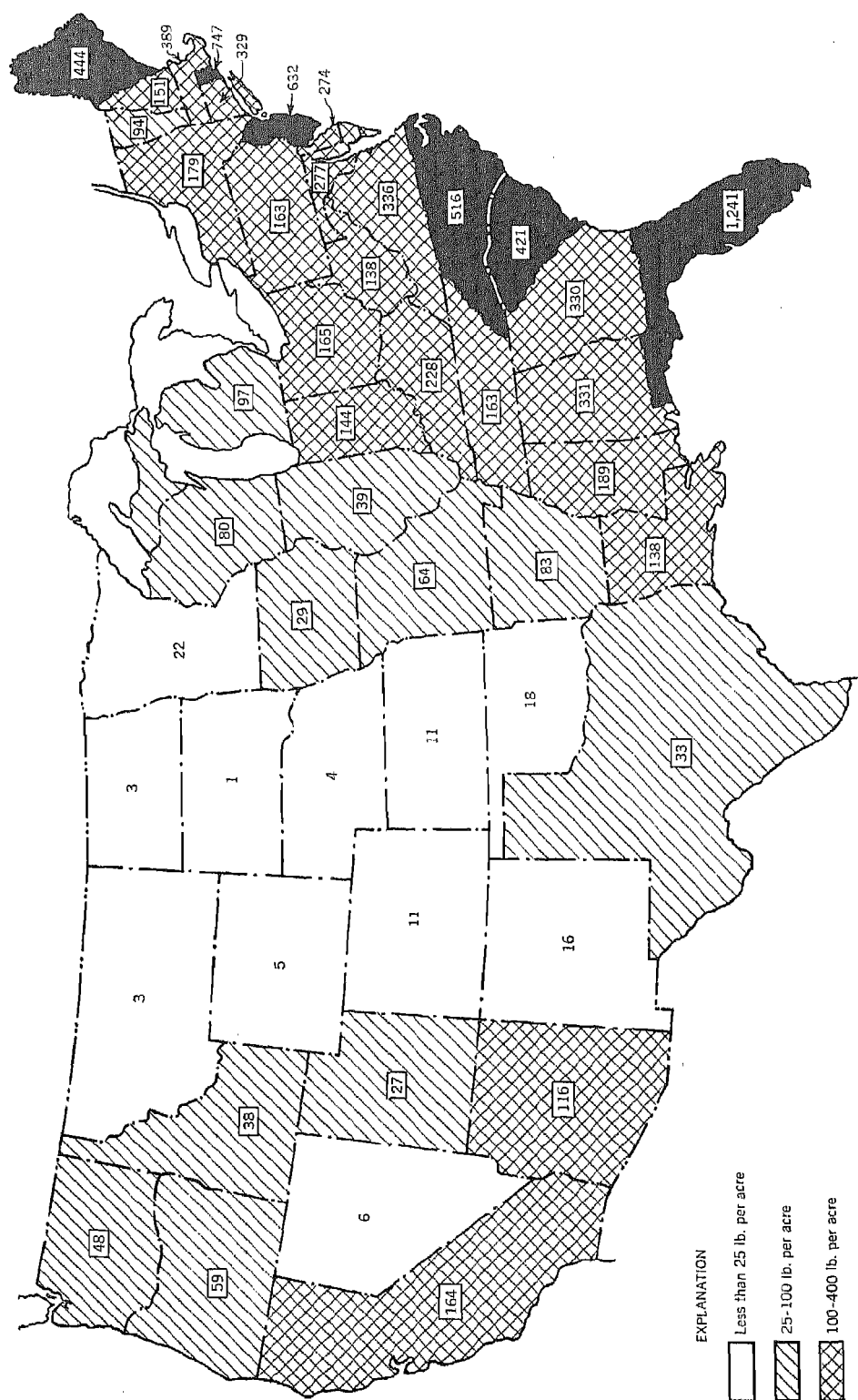


Fig. 1. Fertilizer consumption in pounds per acre of harvested cropland—1948 (12a).

**Silicon** comprises a very large proportion of the ash of some species of plants, particularly of the aerial portions of members of the grass family. Early investigators believed, principally because of the large amounts present in the ash of many species, that silicon is essential. It has been shown that grasses grown in the absence of silica are susceptible to fungus diseases. From this it is supposed that the normal plant is able to ward off such diseases because of the mechanical protection afforded by the silica in the outside walls of the plant. There is also a possibility that silica plays a role in the transportation of iron within the plant in preventing the metal from being precipitated.

The only known function of **chlorine** in plants is as a constituent of anthocyanin pigments.

**Aluminum** is accumulated by some acid-loving plants, but aside from its effects on the color of hydrangea no specific function has been found for it. It is possible that many other elements are required by plants, but in such infinitesimal amounts that present analytical procedures do not permit their isolation.

It is emphasized that each nutrient element works in junction with all the other elements and a deficiency of one or more may throw off balance the entire mineral nutrition of the plant.

### The Need for Fertilizers

A virgin soil supporting a native vegetation can provide that vegetation indefinitely with its mineral nutrient requirements. There is little, if any, loss of the plant foods from this system, since erosion is negligible and mature vegetation dies and returns its nutrients to the soil. But once an agriculture is established upon the soil, the nutrient equilibrium between soil and vegetation is disrupted. Crops produced may be sold off the farm or fed to animals which are sold. Table III shows the amounts of nitrogen, phosphoric acid,  $P_2O_5$ , and potash,  $K_2O$ , contained in some major crops (52). Under continuous cropping, soils are unable to provide optimum amounts of the mineral elements required, and it becomes apparent that supplemental sources of plant nutrients are essential for a prosperous agriculture.

TABLE III. Nutrient Content of Crops.

Crop	Yield per acre	Part of crop	N, lb.	$P_2O_5$ , lb.	$K_2O$ , lb.	Total nutrient content per acre, lb.
Cotton	500 lb.	Lint and seed	38	18	14	70
Tobacco	1500 lb.	Leaves	55	10	80	145
Corn	60 bu.	Grain	57	23	15	95
Wheat	30 bu.	Grain	35	16	9	60
Potatoes	300 bu.	Tubers	65	25	115	205
Sugar beets	15 tons	Roots	55	22	53	130
Tomatoes	10 tons	Fruit	60	20	80	160
Peaches	500 bu.	Fruit	30	15	55	100
Soybeans	25 bu.	Grain	110	35	40	185
Alfalfa	3 tons	All	140	35	135	310
Lespedeza	3 tons	All	130	30	70	230

Coupled with plant-food removal through sale of agricultural products is soil erosion, which, by way of its action in removing the top soil, further depletes the natural supplies of mineral elements available to plant life. A further consideration in the need for fertilizer is the variation in the natural fertility of soils. In general, on the older highly leached soils of the humid, wooded regions of the East and South, large amounts of fertilizer are used, while on the soils of the Corn Belt and the Plains States, formed under reduced rainfall and grass vegetation, smaller amounts are applied. The Southeastern States with their cash-crop agriculture, highly leached soils, and heavy rainfall have long been the largest consumers of plant foods. Figure 1 shows the regional consumption of fertilizer in the U.S.

### Constituents of Commercial Fertilizers

Present-day fertilizers include a large number of grades designed to provide carrying proportions of one or all of the nutrient elements listed above. Fertilizer materials that supply only one of the nutrient elements are sold direct in considerable tonnages and accounted for 26% of the total sales volume in 1948-49. The remaining 74% went to the manufacture of *mixed goods* containing two or more fertilizer elements (54).

As governed by state laws regulating the sale of fertilizers, all plant food must be accompanied by a guarantee showing the percentage of each nutrient element contained for which claim is made by the manufacturer. These are most commonly denoted by figures printed on the fertilizer bag, and it is by these figures that fertilizer grades or analyses, as they are also known, are designated. Ordinarily only nitrogen, phosphorus, and potash in that order are guaranteed. Thus an 8-16-16 grade plant food is one that contains 8% nitrogen, expressed as N, 16% phosphoric acid, expressed as  $P_2O_5$ , and 16% potash, expressed as  $K_2O$ .

However, if the plant food is manufactured for an area particularly deficient in magnesium or the minor elements and the manufacturer chooses to guarantee the content of these elements, they may also appear on the bag following the nitrogen, phosphoric acid, and potash guarantee. Such a mixture used in Florida is 4-10-10-4-2-1, the last three figures referring to magnesium, manganese, and copper, expressed as the oxides. Fertilizers are manufactured in a large variety of ratios of nitrogen, phosphoric acid, and potash in order to meet the requirements of different crops under different soil conditions.

The fertilizer industry of today is largely a chemical industry; in fact, it is the largest of the industries producing heavy chemicals. In the earlier days of the industry, fertilizer mixtures consisted largely of packing-house by-products, animal matter such as tankage, vegetable meals, dried blood, stick, bones, etc. together with trade wastes, with or without the further addition of superphosphate and potash salts. The present-day plant-food mixtures are made largely from chemicals highly and quickly available to plants. Formerly, these materials were gathered from many sections of the world, but at present most of our fertilizer materials are produced in the U.S. The two principal exceptions are calcium cyanamide (Cyanamid) from Canada and natural sodium nitrate from Chile.

In the early days of fertilizer manufacture, mixed goods contained a relatively low content of plant food. This was because the raw materials were of low plant-food analysis. In 1880-1900, organic nitrogen was the cheapest form of nitrogen, and the consumption of these materials exceeded that of any other nitrogen sources. Their nitrogen content was about 5-7%, compared with 40% in the "ammoniating solutions" of today. Superphosphate contained a good deal less available phosphoric acid, about 12% as compared with today's 18-20%, or 45-50% for triple superphosphate. Potash materials, such as kainite, 12.5%  $K_2O$ , and manure salts, 20%  $K_2O$ , were much easier to obtain and much cheaper than the high-grade muriates and sulfates, 50-60%  $K_2O$ , which are plentiful today.

The changes that have taken place in the composition and plant-food content of fertilizer mixtures since 1880 according to the National Fertilizer Association are shown by the formulas given in Table IV. Constantly increasing production of higher-analysis nitrogen, phosphoric acid, and potash raw materials will cause a sharp upward

trend in the next decade. With the increased freight rates of recent years, savings in freight and material handling costs, both by the manufacturer and the consumer, are contributing advantages. As a further impetus a number of states are considering legislation which would limit the grades sold to high-analysis mixtures. Much higher analyses would have been the rule in the 1940-1950 period, if it had not been for foreign commitments for U.S.-produced nitrogen together with the war-induced demand for domestic consumption. As it was, the available raw materials had to be spread out into a large tonnage of lower analyses.

TABLE IV. Average Plant-Food Content of Mixed Fertilizers in the U.S.

Year	Plant-food content, %:				Year	Plant-food content, %:			
	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	Total		N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	Total
1880	2.40	9.10	2.00	13.50	1945	3.91	8.57	7.45	19.93
1900	2.00	9.40	2.50	13.90	1947	3.85	10.57	6.90	21.32
1920	2.30	9.20	2.40	13.90	1948	3.90	10.79	7.08	21.77
1930	3.10	9.80	5.00	17.90	1949	3.99	10.78	7.78	22.55
1940	3.76	9.61	6.37	19.74					

A total of 41 grades of mixed fertilizers represent 90% of the total tonnage of mixtures sold. Actually in 1948 and 1949 there were 894 specified grades sold in the U.S. (54).

### Rates of Fertilizer Application

Rates of application of mixed plant foods are dependent upon: (1) the natural fertility of the soil; (2) the crops being grown; (3) other soil management practices (use of animal manures, and use of nitrogen-supplying legume crops in a rotation); (4) the climate; and (5) economic factors.

It is obvious that on soils of high natural fertility, smaller applications of plant foods are necessary than on poor soils. Crops with a high acre value, such as truck crops, are much more heavily fertilized than such field crops as small grains or corn. The use of animal manures, which have an average analysis of 0.5% N, 0.25% P<sub>2</sub>O<sub>5</sub>, and 0.5% K<sub>2</sub>O, returns an appreciable quantity of plant food to the soil. According to the U.S. Department of Agriculture, more than 3,000,000 tons of plant nutrients are returned annually. Legumes, which through the action of symbiotic bacteria in the root nodules, obtain most of their nitrogen directly from the air instead of from the soil, are among the most valuable plants in an agricultural economy. Their use in a rotation provides a source of cheap, slowly available nitrogen for the succeeding crop, though supplemental applied nitrogen in mixed goods or top dressings is usually recommended.

Climate is of importance in the amounts of plant food used because in humid climates leaching removes large quantities from the soil, while in dry climates, where there is little or no downward movement, the amount of plant food used is governed by the amount of moisture available to crops. A low soil-moisture supply may result in too concentrated a soil solution if heavy applications of plant food are used. Economic factors also govern the rates of application, since in years of agricultural prosperity there is naturally greater fertilizer usage. The extreme ranges and rates of plant-food application are from 100 to 200 lb. per acre on small grains and pastures, to over 2000 lb. per acre on potatoes, truck crops, and citrus crops.

### Methods of Fertilizer Application

There are five general methods of placement for application of fertilizer: (1) broadcasting on the surface of the soil—which may or may not be followed by plowing under the fertilizer; (2) shallow drilling; (3) side-band placement to one side of and below the seed level; (4) plow-sole placement, where a continuous band of plant food is placed in the bottom of the plow furrow; and (5) application in irrigation water (41).

Fertilizers are broadcast on pastures, in orchards, and when fitting the land for very heavily fertilized truck crops. Shallow drilling is practiced with small grain crops. At the time oats, rye, and barley are seeded, an attachment on the grain drill places the plant food one or two inches deep in contact with the seed.

Liquid anhydrous ammonia is used in the Mississippi Delta region for side dressings on cotton and corn as a source of nitrogen. It is also finding limited use elsewhere in the South on pastures and small grains.

For crops planted in rows, such as corn, potatoes, tobacco, cotton, and truck crops, fertilizer attachments on the planting machine place a continuous or interrupted band on one or both sides and the same level or below the seed. In the Middlewest and East, corn also may receive a "plow down" application.

### NITROGEN-CONTAINING MATERIALS

Table V shows the consumption of nitrogen-containing materials in the U.S. since 1880, and Figure 2 (23) shows the relative consumption of various nitrogen-containing materials for the period 1900–1949 according to the National Fertilizer Association.

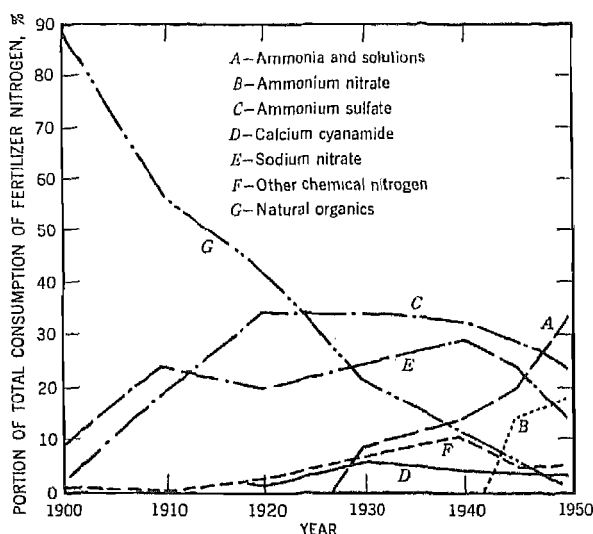


Fig. 2. Relative consumption of various nitrogen-containing materials from 1900 to 1949.

The outstanding feature of the nitrogen picture has been the continuous and very marked decrease in the use of low-analysis, high-cost, natural, organic nitrogen materials. These materials supplied 89% of the commercial fertilizer nitrogen in 1900 but only 3% in 1949. Since 1930 important and increasingly large quantities of

nitrogen in the form of anhydrous ammonia and ammoniating liquors containing mixtures of ammonium nitrate-ammonia-water or urea-ammonia-water have been used. There has also been a marked increase in the production of solid ammonium nitrate since 1942.

TABLE V. Consumption of Fertilizer Nitrogen in the U.S.

Year	Consumption, tons	Year	Consumption, tons
1880.....	18,800	1940.....	413,100
1900.....	71,800	1945.....	595,000
1920.....	227,800	1947.....	745,000
1930.....	375,800	1948.....	824,000

The amount of nitrogen-containing materials used during the 1948-49 season for agricultural purposes in the U.S. is shown in Table VI (13). Approximately 68% of the 1948-49 nitrogen supply was in solid and 32% in liquid forms. Of the former, approximately 70% represented domestic production and 30% imports. Except for a small quantity received from Norway, the 1948-49 imports were roughly one-half from Chile (sodium nitrate) and one-half from Canada (Cyanamid).

TABLE VI. Nitrogen-Containing Materials Used in Agriculture in the U.S., 1948-49.

Type and source	Nitrogen, tons
Ammonium nitrate, 32.5% N and over	
Domestic.....	127,000
Imported.....	41,000
<i>Total ammonium nitrate.....</i>	<i>168,000</i>
Ammonium sulfate, 20.5% N	
Domestic, by-product.....	171,000
Domestic, synthetic.....	55,000
Imported.....	16,000
<i>Total ammonium sulfate.....</i>	<i>242,000</i>
Nitrogen compounds, other	
Domestic sodium nitrate, ammonium phosphate, ammonium nitrate-lime, urea mixtures.....	93,000
Imported calcium cyanamide, ammonium phosphate, calcium nitrate.....	41,000
<i>Total other nitrogen compounds.....</i>	<i>134,000</i>
Sodium nitrate, imported.....	106,000
Natural organics, domestic and imported.....	30,000
<i>Total solid nitrogen.....</i>	<i>680,000</i>
Ammoniating liquors	
Nitrogen solutions: ammonium nitrate-ammonia and urea-ammonia.....	240,000
Ammonia for ammoniation, anhyd. and aq.....	30,000
<i>Total ammoniating liquors.....</i>	<i>270,000</i>
Ammonia for direct application: anhyd., aq., and ammonium nitrate water.....	55,000
<i>Total liquid nitrogen.....</i>	<i>325,000</i>
<i>Total.....</i>	<i>1,005,000</i>



The nitrogen-containing fertilizer materials will be described in three groups: (1) ammonia, ammoniating liquors, ammonium salts, and nitrates; (2) other synthetic nitrogen-containing materials (Cyanamid, urea, and urea-form); and (3) animal and plant by-products (including activated sludge from sewage). Some of these materials are used for direct application to the soil, some as raw materials for mixed goods, and some in both ways.

### Ammonia, Ammonium Salts, and Nitrates

**Ammonia** (*q.v.*) (82.2% N) is used for direct application to the soil and for the manufacture of ammoniated superphosphate (see under "Mixed goods") and ammonium phosphate (see p. 389).

Since 1947, *anhydrous ammonia* has been applied to the soil directly by some farmers in Mississippi, Arkansas, and Louisiana, and to a smaller extent in Alabama, Missouri, Tennessee, and Texas. By means of suitable equipment, it is placed a few inches below the surface of the soil. It combines readily with clay and organic matter. Ammonia neutralizes acids (hydrogen ions) and it may also replace other cations. Even calcareous soils seem to hold ammonia. Anhydrous ammonia is also used in direct application in irrigation water in California and elsewhere.

Anhydrous ammonia is used to a small extent for the manufacture of ammoniated superphosphate, but it supplies less than 3% of the total nitrogen used in mixed fertilizers.

**Ammoniating Solutions.** During 1927-28, ammoniation of superphosphate with aqueous ammonia solution (25%  $\text{NH}_3$ ) produced at coking plants, was started on a commercial scale by several concerns. In 1929, relatively cheap synthetic liquid anhydrous ammonia was used by a few concerns. The consumption of free ammonia in fertilizer mixtures increased from 5,000 tons in 1928 to 40,000 tons in 1930. In late 1929 a solution of ammonium nitrate in ammonia plus water was used for ammoniating about 100 tons of superphosphate. After 1930 the amount of straight anhydrous ammonia and aqua ammonia for ammoniation decreased somewhat, and the use of aqueous ammonia solutions plus ammonium nitrate or aqueous ammonia solutions plus urea became firmly established.

Composition and Properties of Various Ammoniating Solutions.

	Solution <sup>a</sup>			Du Pont UAL solution <sup>b</sup>				
	I	II	III	A	B	C	D	37
Total nitrogen, %	40.6	40.8	37.0	45.5	45.5	37.0	37.0	37.1
Anhyd. ammonia, %	21.7	26.0	16.0	36.8	30.6	29.8	25.0	25.0
Nitrate nitrogen, %	11.37	9.65	11.68	—	—	—	—	—
Total ammonia nitrogen, %	29.24	31.18	25.35	—	—	—	—	—
Urea nitrogen, %	—	—	—	15.1	20.2	12.3	16.4	9.1
Insol. organic nitrogen, %	—	—	—	—	—	—	—	74
Water, %	13.3	18.5	16.6	24.8	17.6	38.6	32.8	24.8
Vapor pressure, approx., at 100°F., p.s.i.	10 <sup>c</sup>	16 <sup>c</sup>	1 <sup>c</sup>	64	50	20	16	20
Crystn. temp. of salt or urea, approx., °F.	23	13	48	5	34	6	34	34
Sp.gr., approx., at 60°F.	1.142	1.079	1.182	0.99	1.06	1.00	1.05	1.08

<sup>a</sup> Water-anhydrous ammonia-ammonium nitrate solutions.

<sup>b</sup> Water-anhydrous ammonia-urea solutions, except UAL 37 which also contains formaldehyde.

<sup>c</sup> At 104°F.

Several manufacturers are producing ammoniating solutions containing water, free ammonia, and ammonium nitrate, and selling them under their own trade names, such as Barrett Standard Nitrogen Solutions, Spensol Solution, Phillips Nitrogen Solutions, and Lion Nitrogen Solutions. E. I. du Pont de Nemours & Company manufacture solutions containing water, anhydrous ammonia, and urea and also a solution containing water, anhydrous ammonia, urea, and formaldehyde. The latter solution when added to ordinary or triple superphosphate mixtures forms some water-insoluble organic nitrogen compounds. See the accompanying table.

*Ammonia liquor* (aqua ammonia or B-liquor, 24.6% N) is used to some extent in the manufacture of mixed goods.

Ammonia liquor was the first ammonia-containing solution used in the manufacture of ammoniated superphosphate, but at present specially prepared ammoniating solutions are more largely used.

**Ammonium Nitrate**,  $\text{NH}_4\text{NO}_3$  (32.5–33.5% N) (see Vol. 1, p. 817). Most of the ammonium nitrate used as fertilizer in the U.S. is applied directly to the soil; it is also used in ammoniating solutions containing ammonium nitrate for the manufacture of mixed fertilizers.

Ammonium nitrate shows a marked tendency to cake and to absorb moisture from the air when the humidity exceeds 60% at 86°F. The tendency of granular ammonium nitrate to cake can be greatly reduced by coating the dry material with 0.5–1.0% of a rosin–paraffin–petrolatum water-repellent mixture, followed by 4–5% of a conditioning agent such as kieselguhr, kaolin, clay, or tricalcium phosphate and storing in moistureproof bags. If ammonium nitrate is to be used in dry sections of the country, the use of wax coatings is unnecessary. Pure ammonium nitrate has a total nitrogen content of 35%. The conditioning agents applied in commercial practice reduce the guaranteed nitrogen content to 32.5–33.5% N.

Ammonium nitrate can be both a fire and an explosion hazard. In 1949, the Spencer Chemical Company reported a fire which destroyed over 2,700,000 lb. of their fertilizer-grade ammonium nitrate. The leased storehouse adjoined another in which the fire originated and in which another concern stored bagged alfalfa meal. Temperatures in excess of 1980°F. were believed to have been obtained. No blast occurred. There are other recorded instances in which relatively large amounts of ammonium nitrate in contact with organic matter caused intensely hot fires without causing explosions. The possible explosive character of ammonium nitrate is discussed in Vol. 1, p. 823. See also *Explosives*.

In order to guide the industry in the handling of this material and in the hazards connected with it, the U.S. Department of Agriculture lists the following (10):

*Fire Hazard.* Ammonium nitrate in bulk offers much the same fire hazard as sodium nitrate; that is, mostly an indirect hazard from the liberation of oxygen at moderately high temperatures, which tends to increase the intensity and spread of a fire.

“Readily oxidizable metallic powders in contact with wet ammonium nitrate may result in spontaneous combustion. Zinc powder seems to be most reactive under such conditions.

“The presence of 5 per cent aluminum, iron, or zinc powder with dry material does not appreciably increase its inflammability. Experiments with 5 per cent charcoal produced no burning by direct contact with a flame, but with 11 per cent charcoal it burned with very small flame. With 5 per cent wood powder decomposition occurred without flame.

“Organic or other easily oxidizable substances impregnated or in contact with ammonium nitrate produce violent combustion on ignition.

“Copper is the only common metal that reacts appreciably with molten ammonium nitrate,

producing nitrite, which is less stable than nitrate, and increasing the tendency to violent conflagration or explosion.

"Decomposition of ammonium nitrate at temperatures below 100°C. into ammonia and nitric acid produces a greater fire hazard under some conditions in mixtures than is found in sodium nitrate."

Bags that have contained ammonium nitrate should not be piled even temporarily in or near a wooden building, as they are flammable. Bags should be burned promptly after emptying.

Bearing in mind that ammonium nitrate is explosive and supports combustion, it should be handled in such a way as to avoid conditions that would make it dangerous. More than ordinary caution should be practiced along the lines indicated, but no violent reactions need be anticipated from impacts, jars, or friction, which must be avoided with more sensitive explosives.

Should ammonium nitrate be involved in a burning building or in a fire with other combustible material, ordinary fire-fighting methods should be used to extinguish it. Water is generally the most convenient and effective; it will exert its usual cooling effect in extinguishing a fire.

Fumes from burning ammonium nitrate are extremely toxic and should not be inhaled. Persons who fight fires in which these chemicals are concerned should wear gas masks.

The U.S. Department of Agriculture further lists these precautions to be observed in handling and storage of ammonium nitrate under farm conditions (67).

"1. Do not smoke or permit smoking or the use of open flames in or near space where ammonium nitrate fertilizer is stored.

"2. Keep ammonium nitrate away from explosives and combustible materials of all kinds, especially gasoline, oils, paints, straw, hay, cloth, paper, shavings, scraps of lumber, etc.

"3. Store ammonium nitrate in a well-ventilated building to permit ready escape of gases in the event of fire. If large quantities are to be stored for a considerable period, they should be placed in a building removed by several hundred feet from other farm buildings.

"4. Do not store ammonium nitrate near steam pipes or near electric wiring.

"5. Clean up spilled ammonium nitrate at once and discard if it has become mixed with combustible material. Do not return such contaminated material to the bag. It is safest to discard all spilled ammonium nitrate. This may be done, however, by spreading it on the land, where it will benefit crops.

"6. Destroy promptly empty bags that have contained ammonium nitrate. This does not mean that bags emptied in the field cannot be allowed to lie in the open away from buildings until it is convenient to destroy them."

See also *Fire prevention and extinction*.

**Other Nitrates.** *Sodium nitrate* (see *Sodium compounds*) is used for direct application; only a small amount is now used in fertilizer mixtures. The synthetic product, made from nitric acid and soda ash, contains 16.4% N, and is 99.48%  $\text{NaNO}_3$ . Chilean "nitrate of soda" is produced as the old-style crystalline form (guaranteed analysis 16% N) and as the Champion-Brand pellet form (about 16.2% N).

"*Nitrate of soda potash*" is a commercial product containing nitrates of sodium and potassium. It is a combination of Chilean sodium nitrate and potassium nitrate produced from caliche, containing a high percentage of potassium nitrate. It is usually guaranteed to contain not less than 15% N and 14%  $\text{K}_2\text{O}$ . The amount imported is relatively small.

*Potassium nitrate* is imported in small quantities, but the material is too expensive for general fertilizer use. Commercial grades contain about 95%  $\text{KNO}_3$ , equivalent to about 13.2% N and 44%  $\text{K}_2\text{O}$ .

*Calcium nitrate* (nitrate of lime) is imported in small quantities for direct application. The fertilizer grade is essentially  $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , but contains also sufficient ammonium nitrate to supply 1% N in ammonia form. It is usually sold in granular form and contains about 18.5% total nitrogen and 28.0% water-soluble lime (as  $\text{CaO}$ ).

*A-N-L-Brand* fertilizer compound is a trade name for a fertilizer material being produced at Hopewell, Virginia. It is a mixture of ammonium nitrate and finely

pulverized dolomite made in pellet form. Its guaranteed analysis is: nitrate nitrogen, 10.2%; ammonia nitrogen, 10.3%; total nitrogen, 20.5%; calcium oxide, 9.0%; magnesium oxide, 7.0%.

Similar material with the trade name *Cal-Nitro* formerly imported from Europe is now produced domestically. A limited amount is used in the manufacture of mixed fertilizers but the greater portion finds use as a nitrogen side dressing.

**Ammonium Sulfate**,  $(\text{NH}_4)_2\text{SO}_4$  (20.6% N) (see Vol. 1, p. 778). Until 1948, most ammonium sulfate was made from ammonia gas, obtained from coke ovens, and sulfuric acid. But in the late months of 1949 and early months of 1950, the tonnage manufactured from synthetic ammonia equalled that from the coke-oven industry. Ammonium sulfate is one of the important sources of nitrogen in mixed fertilizers, being the principal source for factories where only "dry" mixing is practiced. Its use as a separate material for direct application to the soil is rather limited.

**Ammonium Phosphates** (see *Phosphoric acid*). Pure *monoammonium phosphate*,  $\text{NH}_4\text{H}_2\text{PO}_4$  (12.17% N, 61.71%  $\text{P}_2\text{O}_5$ ), is made by mixing pure phosphoric acid (usually made by the electric furnace process) and ammonia in proper proportions and evaporating the solution. A small tonnage is used for agricultural purposes where a completely water-soluble product is desired.

The principal ammonium phosphate products used as fertilizers and containing the crude salt are 11-48-0 with 11% N and 48%  $\text{P}_2\text{O}_5$ , and 16-20-0 containing 16% N and 20%  $\text{P}_2\text{O}_5$ . The latter product, although referred to as ammonium phosphate, is actually a mixture of monoammonium phosphate and ammonium sulfate. One of the large producers of these two products is the Consolidated Mining & Smelting Company of Canada at Trail, B.C., which has published the following information (2):

Average daily production of 11-48-0 and 16-20-0 is 200 and 400 tons, respectively. Crude phosphoric acid produced by the wet process is used in three units in parallel. Two units ordinarily produce 16-20-0 ammonium phosphate and the third 11-48-0. With the phosphoric acid section treating 650 tons of phosphate rock per day, reasonably balanced operation can be obtained. The equipment installed on each unit is identical. It is possible on short notice to swing operations from one ammonium phosphate product to the other (see Fig. 3).

*Ammonium Phosphate, 11-48-0.* Evaporated phosphoric acid is pumped continuously by a stainless-steel centrifugal pump to a hard-lead splitter box equipped with a weir to control the flow. The overflow is carried from the splitter box back to the storage tank. The hard-lead measuring box is installed in series with the splitter box for checking the rate of acid delivery. The measured acid then flows by gravity through a hard-lead line to the first reaction agitator.

The three reaction agitators are constructed of wood and are lead- and acidproof-brick-lined. They are placed in a series with gravity overflow out of the top of each. The first agitator is 8 ft. in diameter and 9 ft. in height. In it 80% of the neutralization with ammonia is carried out. The remaining two reaction agitators are 6 ft. in diameter and 7 ft. high. Each is equipped with stainless-steel shafts and propeller. Stainless-steel pipes, 3 in. in diameter, carry ammonia gas into each agitator.

Gaseous ammonia at 12 p.s.i.g. passes into the first agitator. The slurry continually overflows into the second agitator, and the remainder of the reaction with ammonia takes place here. The third agitator can be used for final adjustment. Experienced operators rarely find it necessary to adjust after the second agitator.

The reaction is strongly exothermic and the temperature rises rapidly to 100-

105°C. in the second agitator, cooling by evaporation in the third agitator to 90–95°C. Large volumes of steam from the reaction agitators are ventilated by an exhaust fan and wood duct to a scrubber tower. A dilute solution of sulfuric acid (3–4%) is circulated continuously through the tower countercurrent to the gas flow of 25,000 cu.ft. per minute. Traces of free ammonia gas are thus recovered from the agitators before exhausting to waste. The scrubber liquor is returned with the feed phosphoric acid to the first reaction agitator. The slurry from the third agitator flows through a launder into the blunger.

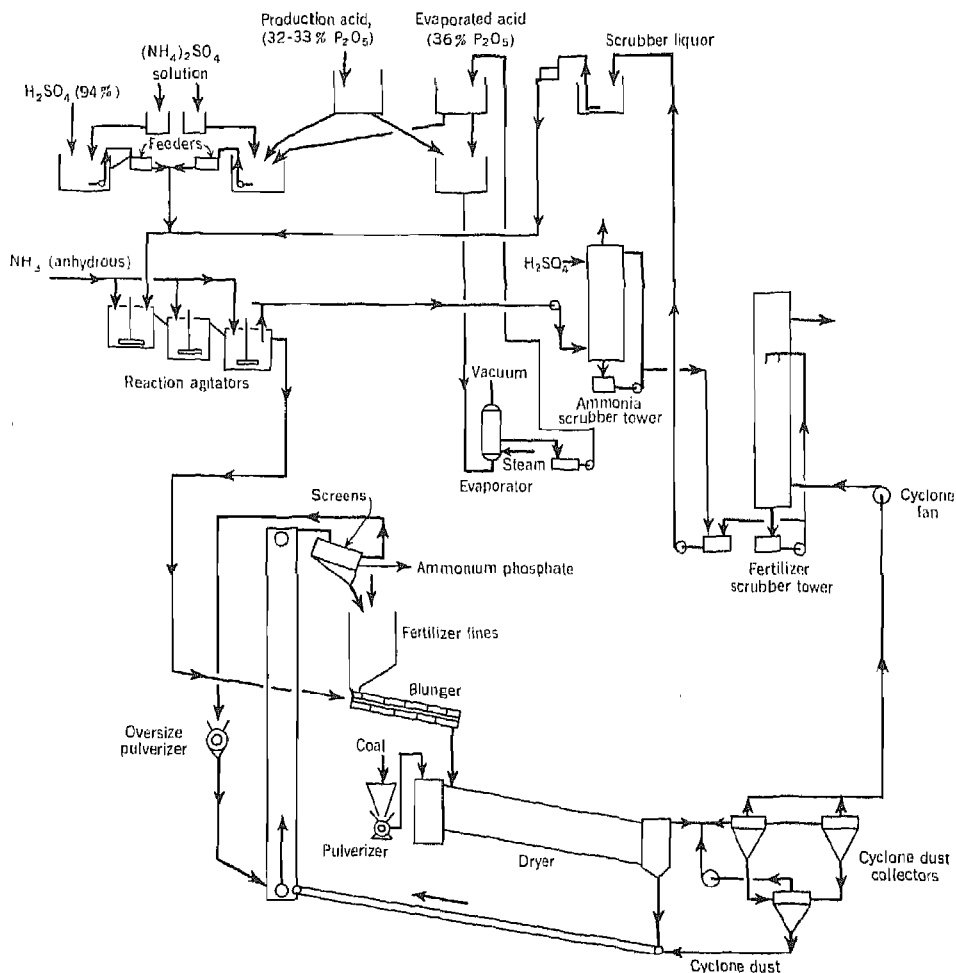
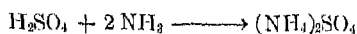


Fig. 3. Manufacture of ammonium phosphate (2).

The principal reaction is the formation of monoammonium phosphate from phosphoric acid and anhydrous ammonia:



A small quantity of sulfuric acid present in the phosphoric acid reacts to form ammonium sulfate:



The blunger is a large mechanical mixer with two horizontal shafts each fitted with intergeared blades. Its active mixing length is 7.5 ft. The hot ammonium phosphate slurry meets a large excess of granular finished product of screen size too small for shipment. The fines are continuously screened out of the finished product and are returned to the blunger. Mixing of slurry and the fine dry granules is rapid. Each granule receives a coating of the slurry resulting in the general build up of particle size. The consistency of the mixture discharging from the blunger should be such that it "balls up" readily when a sample is squeezed by hand.

The material discharging from the blunger goes by gravity to a rotary dryer. The temperature of the dryer is automatically controlled by maintaining the discharge gas at 100°C. Dust from the dryer is recovered by a cyclone dust collector, from which the air is exhausted through a scrubber. The collected dust and the dryer product are fed to a double-deck screen. The upper screen surface is approximately 7 mesh and the lower screen 12 mesh. The oversize is scalped off and gravitates to the hammer mill from where it is returned to the screen. The -7 to +12 mesh finished product is carried by a belt conveyor to storage bins. The undersize, -12 mesh material, is returned to the blunger.

*Ammonium Phosphate, 16-20-0.* Unevaporated normal production acid (32-33%  $P_2O_5$ ) is measured out by acid feeders and flows into the first reaction agitator. Sulfuric acid (94%) is measured separately by acid feeders and flows into the first reaction agitator. Control of the ratio of phosphoric and sulfuric acids is correlated to give a finished product analyzing 16% N and 20%  $P_2O_5$ . A proportion of saturated ammonium sulfate solution is used with the approximate quantity of sulfuric acid. Ammoniation is done in exactly the same way as in the ammonium phosphate 11-48-0 process—80% in the first agitator and the balance in the second. This reaction is also strongly exothermic with the slurry reaching a temperature of 110°C. With minor exceptions the operation is similar to the 11-48-0 ammonium phosphate process previously described. The circulating fines are built up in size, dried in a rotary dryer, and screened over double-deck vibrating screens.

Most of the 11-48-0 and 16-20-0 is used for direct application on soils not deficient in available potash; only a limited quantity is used in the manufacture of complete fertilizer.

*Diammonium phosphate,  $(NH_4)_2HPO_4$ ,* is not used in commercial quantities as a fertilizer material in the United States. The Tennessee Valley Authority at Wilson Dam, Alabama, has reported the production on a pilot-plant scale of diammonium phosphate fertilizer containing 21% N and 54%  $P_2O_5$  (bone-dry basis) from anhydrous ammonia and electric-furnace phosphoric acid. A continuous, single-step, saturator-type process similar to commonly used methods for manufacturing by-product ammonium sulfate is employed by the TVA. The product was substantially pure ammonium phosphates with diammonium phosphate predominating; the monocalcium phosphate content varied from a few tenths to 4-5%. The product showed only negligible loss of ammonia under normally occurring conditions of temperature and humidity. There was evidence that the diammonium phosphate suffered significant ammonia loss when mixed with strong basic materials such as calcium cyanamide and lime or with high proportions of certain other ammonia compounds such as urea and ammonium nitrate.

### Other Synthetic Nitrogen-Containing Fertilizers

**Cyanamid** (see Vol. 4, p. 664) is a trade-mark for a material containing about 63% calcium cyanamide,  $\text{CaCN}_2$ , 15% calcium oxide,  $\text{CaO}$ , and 12% free carbon (graphite), together with small amounts of miscellaneous impurities derived from the limestone and coke used in its manufacture. It is supplied to the trade in two forms: pulverized, containing 22% N, and granular, containing 21% N. Cyanamid is used for both direct application and in the manufacture of complete fertilizer.

**Urea** (*q.v.*) is used in ammoniating solutions (see under "Mixed goods").

**Urea-Form.** This name was recently applied to a class of urea-formaldehyde reaction products suitable for fertilizer use. Although still in the development stage, these products have promise as a source of slowly available nitrogen. Such products are formed under conditions that will insure the reaction of more than one molecular equivalent of urea per mole of formaldehyde. They usually contain 36-38% N and about 4% moisture, and are much less water-soluble than the chemical nitrogen fertilizers in present-day use. The solubility of the product formed decreases as the acidity increases from pH 7 to pH 2. It has been shown that the rate of availability can be controlled to approximately the nutritional requirements of long-season crops by proper choice of the conditions under which the product is prepared.

**Uramon.** This is a trade-mark for a product containing urea prepared especially for fertilizer use. It is a semigranular compound containing 42% N derived from urea. The granules are coated to reduce the tendency to cake and absorb moisture and to make it more free-flowing. Uramon is used for direct application to the soil and also in the manufacture of mixed fertilizer.

### Animal and Plant By-Products

In the early days of fertilizer manufacture, dried blood, bone meal, fish meal, and hoof meal were important sources of nitrogen. With the development of synthetic nitrogen sources this is no longer so, although *tankage* containing 5-10% N is used in small quantities today as a source of water-insoluble nitrogen. This material includes a number of commercial products derived from animal matter such as leather scraps, hair, feathers, and wool waste, hydrolyzed with steam under pressure, and then dried and ground. Dried blood, bone meal, and fish meal, which in 1900 were important nitrogen sources, today are utilized as protein and mineral supplements in livestock feeds. See *Feeds, animal*.

**Milorganite** is a trade name for the activated sludge manufactured by the Sewerage Commission of the City of Milwaukee. The sludge, containing about 98% water, is filtered by means of vacuum filters, producing a cake containing about 80% water. This cake is dried in rotary dryers, ground, and screened. The average analysis of Milorganite is: moisture, less than 5%; nitrogen, 5.3-6.2%; total phosphoric acid,  $\text{P}_2\text{O}_5$ , 3-4%; and available phosphoric acid,  $\text{P}_2\text{O}_5$ , 2-3%. Most of the material is now used for direct application.

**Plant by-products** are used both as a source of water-insoluble nitrogen and as conditioning agents for mixed fertilizers. Like the animal by-products, they are used only in very small quantities compared with the synthetic nitrogen sources. *Castor pomace* contains 4-7% N. It is the material remaining after the oil has been extracted from castor beans. *Cottonseed meal* with a content of 6.7-7.4% N, 2-3%  $\text{P}_2\text{O}_5$ , and 1.5-2%  $\text{K}_2\text{O}$  is the press cake remaining after cooking and steaming cottonseed in the

extraction of linseed oil. *Garbage tankage* with an analysis of 2.5–3.3% N, 2–5%  $P_2O_5$ , and 0.5–1%  $K_2O$  is the rendered, dried, and ground product derived from rendering kitchen wastes. *Soybean meal* contains approximately 4.5% N and is the ground press-cake by-product of oil extraction. *Tobacco stems*, *cocoa shell meal*, *rice hulls*, *peanut hull meal*, and *peat* all contain a small amount of nitrogen, phosphoric acid, and potash, but are used as conditioning agents rather than major sources of plant nutrients.

### PHOSPHORIC ACID-CONTAINING MATERIALS

Justus von Liebig's famous report of 1840 "Organic Chemistry in Its Application to Agriculture and Physiology" recommended grinding bones to a fine powder and then treating them with sulfuric or hydrochloric acid as a practical method for obtaining phosphates in a form easily assimilated by plants. The English farmer Fleming was the first to follow Liebig's suggestion. He treated bones with sulfuric acid and sold the resultant product as "German compost." In 1843, Sir John Bennet Lawes

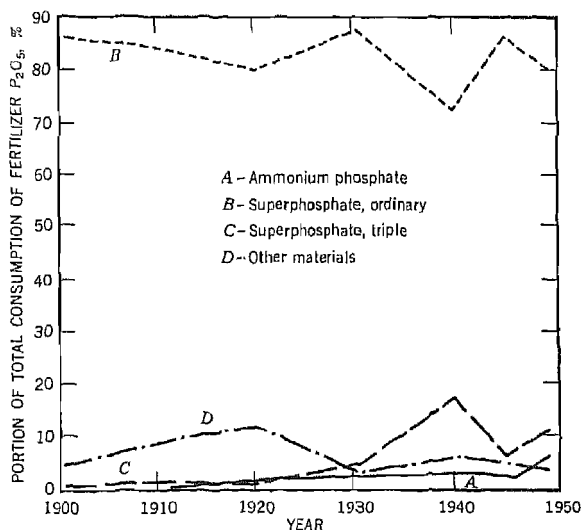


Fig. 4. Relative consumption of various phosphoric acid-containing materials from 1900 to 1949.

and Sir Joseph Henry Gilbert appear to have been the first to treat the mineral phosphate "coprolites" with sulfuric acid. Because of this, Lawes and Gilbert are generally considered the founders of the superphosphate industry. Coprolites or "crag nodules" are the fossilized excrements of animals found in abundance in Suffolk and in Cambridgeshire.

The demand for soluble phosphates for agriculture soon became so great that the supply of bones was totally inadequate to meet it. A search for phosphate revealed large quantities of phosphate-bearing minerals in various parts of the earth. Several large deposits have been discovered since 1900, some very recently. It is reasonable to assume that still more will be found. The known deposits should be adequate to meet man's need for about another 2000 years.

Figure 4 (23) shows the relative consumption of various phosphoric acid-con-



taining fertilizer materials. Tables XIII and XIV give the U.S. and world production of superphosphate.

Phosphate rock is the raw material from which practically all phosphates used as fertilizers are manufactured. Since phosphorus in phosphate rock occurs in mineral forms that are extremely unavailable to plants (see "Phosphate rock") some treatment is necessary to make the phosphorus soluble. Most of the treatments that are used depend on the formation of monocalcium phosphate,  $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  (water-soluble), and some dicalcium phosphate,  $\text{CaHPO}_4$  (ammonium citrate-soluble). It is customary to speak of the "available phosphoric acid" or "A.P.A." of a phosphate fertilizer, referring to the amount of phosphorus, calculated as  $\text{P}_2\text{O}_5$ , that is soluble under certain specified test conditions.

Methods of analysis for available phosphoric acid have been standardized by the Association of Official Agricultural Chemists (1). The most important analyses are for solubility in water and in neutral ammonium citrate solution. Water solubility is determined by fractional exhaustion with successive small quantities of cold water. Ammonium citrate--soluble or citrate-soluble phosphate is determined by subsequent solution in a neutral ammonium citrate solution. Available phosphoric acid is the sum of water- and ammonium citrate-soluble phosphoric acid.

In Europe, water solubility is sometimes determined by one extraction with a large bulk of water. Citrate solubility is determined in an alkaline ammonium citrate (Petermann) solution.

The choice of ammonium citrate as a solvent is purely empirical since the actual availability of phosphates in the soil may vary greatly from one soil type to another. Available phosphoric acid is therefore a generalized term and does not indicate an actual availability to all crops under all soil conditions.

Approximately 80% of phosphoric acid for agricultural purposes is furnished in a product known as superphosphate. This product is manufactured by treating phosphate rock with sulfuric acid, forming a mixture consisting largely of monocalcium phosphate and calcium sulfate, and containing from 18 to 21% A.P.A., depending upon the grade of rock used in the manufacture.

By treating phosphate rock with phosphoric acid instead of sulfuric acid, products containing from 43 to 50% A.P.A. can be obtained. The names double superphosphate, treble superphosphate, triple superphosphate, and concentrated superphosphate have all been applied to such products and although some writers attempt to make distinctions among the names, in practice they are often used synonymously. All of these products are sometimes referred to as varieties of superphosphate so that the term "superphosphate" may or may not include the high-analysis products. They will all be referred to here as triple superphosphate. This product supplies about 11% of the phosphoric acid for agricultural purposes.

The phosphoric acid used for making triple superphosphate can be obtained by various processes. Acid of high purity is not necessary for triple superphosphate manufacture; therefore the bulk of phosphoric acid so utilized is made by the "wet process," in which phosphate rock is treated with sufficient sulfuric acid to convert it into phosphoric acid and calcium sulfate, which is removed by filtration. Phosphoric acid can also be made by burning phosphorus and absorbing the phosphorus pentoxide in water; the phosphorus is produced from phosphate rock by the electric-furnace or blast-furnace method. (See *Phosphoric acids*.) Phosphoric acid is also used for making monoammonium and diammonium phosphate. A mixture of phosphoric and sul-

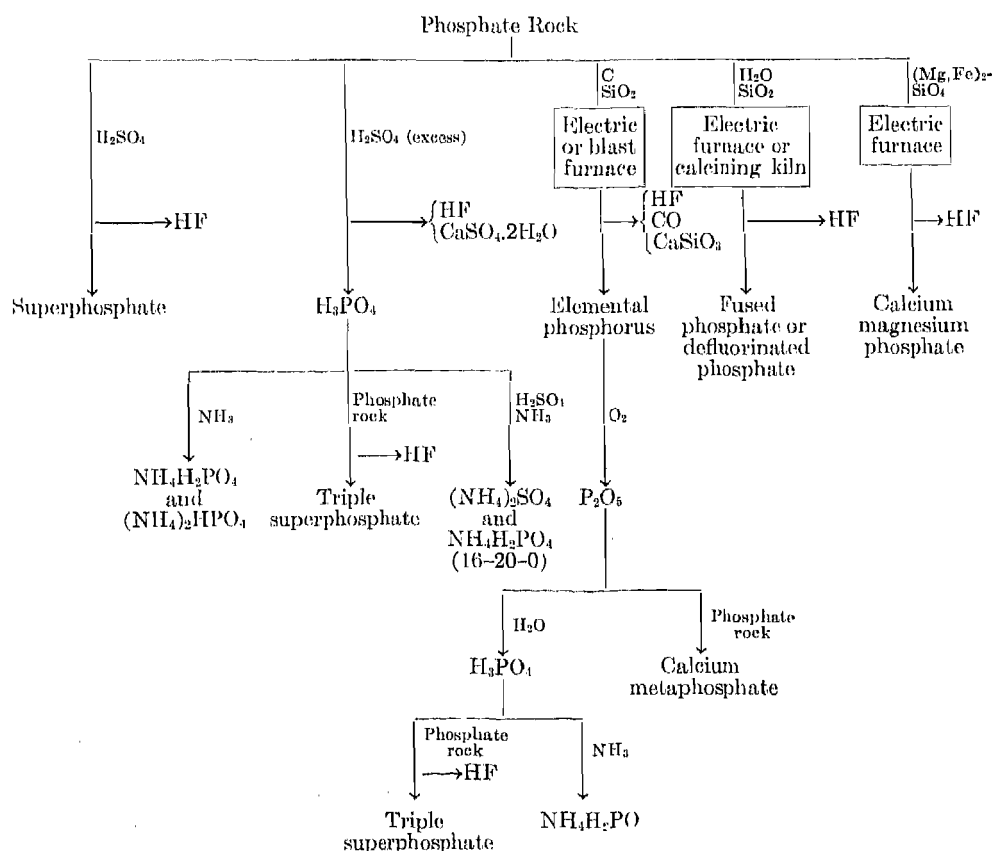
furic acids treated with ammonia gives 16-20-0 which contains monoammonium phosphate and ammonium sulfate (see p. 389).

Other fertilizer products are made from phosphate rock by furnace methods. Defluorinated phosphate rock is produced by calcining phosphate rock without fusion in the presence of steam. Fused tricalcium phosphate is made by fusion of phosphate rock and silica,  $\text{SiO}_2$ ; water vapors produced by combustion of the fuel effect the defluorination. Calcium metaphosphate contains more than 60% available phosphoric acid and is made by blowing pulverized phosphate rock into a combustion chamber where phosphorus is burning to phosphorus pentoxide. Molten calcium metaphosphate collects as a slag at the bottom of the combustion chamber. Calcium magnesium phosphate is made by treating a mixture of phosphate rock and olivine,  $(\text{Mg,Fe})_2\text{SiO}_4$ , in an electric furnace.

The flow diagram shows various methods for making fertilizer phosphates from phosphate rock.

Basic slag (see *Iron; Steel*) has some use as a fertilizer material in the U.S. About 40,000 tons is produced annually by the open-hearth furnaces in Birmingham, Alabama. It is used as a source of phosphate and liming material for direct application to the soil near its point of origin. It analyzes approximately 10-25%  $\text{P}_2\text{O}_5$ , 40-50%  $\text{CaO}$ , 5-15%  $\text{SiO}_2$ , and small amounts of iron, alumina, magnesia, sulfur, manganese,

Flow Diagram: Fertilizer Phosphates from Phosphate Rock.



etc. According to the A.O.A.C. specifications it must contain not less than 12% of  $P_2O_5$ , and not less than 80% of it must be soluble in 2% citric acid solution according to the Wagner method.

### Phosphate Rock

The mineral phosphates used by the fertilizer industry are commonly referred to as phosphate rock. Distribution of phosphate rock of sufficiently high phosphorus content to be worked profitably under present conditions is estimated as shown in Table

TABLE VII. World Resources of Phosphate Rock, 1944.

Location	Resources, tons
Tunisia.....	1,500,000,000
Algeria.....	1,016,500,000
Egypt.....	179,000,000
Morocco.....	1,000,000,000
Europe (excluding U.S.S.R.).....	435,126,000
U.S.S.R.....	7,568,000,000
Palestine.....	4,000,000
Canada.....	181,000
Mexico.....	214,500,000
Brazil.....	573,000,000
Ocean and Nauru Islands.....	282,245,000
Makatea Island.....	10,000,000
Christmas Island.....	50,000,000
Japan and Micronesian Islands.....	28,984,000
China.....	2,400,000
Indo-China.....	55,000
India.....	10,128,000
Indonesia.....	1,000,000
Other foreign deposits.....	2,496,000
<i>Total foreign deposits.....</i>	<i>12,877,615,000</i>
U.S.....	13,503,514,000
<i>Total world reserves.....</i>	<i>26,381,129,000</i>

Source: reference (44a).

TABLE VIII. U.S. Production of Phosphate Rock, Long Tons.

	Year	
	1947	1948
Production (mined).....	9,110,989	9,388,100
Sold or used by producers:		
Florida.....	6,482,027	6,539,258
Land pebble.....	6,314,077	6,421,725
Soft rock.....	88,620	69,335
Hard rock.....	79,330	48,198
Tennessee.....	1,411,884	1,307,507
Idaho.....	845,045	484,375
Montana.....	236,229	248,683
Wyoming.....	51,845	138,946
<i>Total U.S.....</i>	<i>9,027,030</i>	<i>8,668,769</i>

Source: *Mineral Market Rept.*, MMS No. 1761, U.S. Dept. Interior, 1949.

VII. Tables VIII and IX show, respectively, the U.S. and world production of phosphate rock.

TABLE IX. Estimated World Production of Phosphate Rock, Long Tons.

Location	Year	
	1938	1946
<b>Europe</b>		
Belgium.....	75,000 <sup>a</sup>	72,521
Eire.....	—	14,424
France.....	82,000 <sup>a</sup>	50,000
Germany.....	3,221	—
Poland.....	13,000 <sup>a</sup>	10,000 <sup>a</sup>
Rumania.....	970	—
U.S.S.R.....	2,363,012 <sup>a</sup>	1,600,000 <sup>a</sup>
Spain.....	24,953	12,385
Sweden.....	6,192	42,244
<i>Total Europe.....</i>	<i>2,568,348</i>	<i>1,801,574</i>
<b>Africa</b>		
Algeria.....	584,500	594,843 <sup>b</sup>
Tunisia.....	2,034,200	1,777,736 <sup>b</sup>
Morocco.....	1,487,000	2,882,333 <sup>b</sup>
Egypt.....	458,400	294,735
South Africa.....	—	30,000 <sup>a</sup>
Madagascar.....	5,691	—
Tanganyika.....	106	279
<i>Total Africa.....</i>	<i>4,569,897</i>	<i>5,579,926</i>
<b>America</b>		
U.S.....	3,922,244	7,283,540
Curaçao.....	104,470 <sup>b</sup>	75,046 <sup>b</sup>
Chile.....	24,000	40,000 <sup>a</sup>
Brazil.....	—	4,000 <sup>a</sup>
Canada.....	200	—
<i>Total America.....</i>	<i>4,050,914</i>	<i>7,402,586</i>
<b>Asia</b>		
India.....	23	—
Indonesia.....	33,111	10,000 <sup>a</sup>
Indo-China.....	37,339	10,000 <sup>a</sup>
China.....	—	—
Christmas Island.....	162,417 <sup>b</sup>	33,071 <sup>b</sup>
Transjordan.....	—	8,500
<i>Total Asia.....</i>	<i>232,890</i>	<i>61,571</i>
<b>Oceania and Pacific Ocean</b>		
Micronesian Islands.....	255,967	100,900 <sup>a</sup>
Australia.....	498	—
Makatea.....	102,940 <sup>b</sup>	232,512 <sup>b</sup>
Ocean and Nauru Islands.....	1,158,849	88,240
New Caledonia.....	5,000	—
<i>Total Oceania and Pacific.....</i>	<i>1,523,254</i>	<i>420,752</i>
<i>Total world production.....</i>	<i>12,945,303</i>	<i>15,266,409</i>

<sup>a</sup>Estimated.

<sup>b</sup>Delivered.

Source: International Superphosphate Manufacturers Association, London.

Table X (25,53) shows that various naturally occurring phosphates contain, in addition to the plant-nutrient elements phosphorus and calcium, also magnesium, iron, potassium, and manganese in minor amounts. Traces of copper, zinc, and molybdenum needed for plant nutrition are also found in most natural phosphates. The Florida land-pebble rock also contains about 10 p.p.m. of iodine. The phosphate content of at least some of the phosphate deposits is in part due to the formation of soluble phosphates from decomposing guano of fish-eating birds and leaching to underlying deposits of limestone. Fish and other animal remains also played a part in the formation of deposits. The reactions that took place were probably complex. During the intermediate stages, the phosphates probably existed as hydroxylapatite or calcium hydroxyphosphate,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  or  $[\text{Ca}_3(\text{PO}_4)_2]_3 \cdot \text{Ca}(\text{OH})_2$ , and carbonate-apatite or calcium carbonate phosphate,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3)$  or  $[\text{Ca}_3(\text{PO}_4)_2]_3 \cdot \text{CaCO}_3$ .

TABLE X. Approximate Composition of Dried Phosphate Rock Used in the Manufacture of Ordinary and Triple Superphosphate.

Constituent	Composition, %		
	Florida land-pebble rock	Tennessee brown rock	Idaho, Montana, Wyoming rock
$\text{P}_2\text{O}_5$	30-36	30-36	27-33
$\text{Fe}_2\text{O}_3$	0.7-2.6	2.2-3.4	0.5-2.1
$\text{Al}_2\text{O}_3$	0.7-1.1	1.2-2.7	0.5-1.9
$\text{CaO}$	46-50	42-49	43-47
$\text{MgO}$	0.04-0.6	0.02-0.3	Trace-0.3
F	3.8-4.0	3.2-3.8	2.9-6.9
Cl	0.003-0.03	0.005-0.07	0.01-0.03
I	0.0008-0.002	0.0009-0.003	0.0001-0.0003
$\text{SiO}_2$	2-10	5-9	5-17
$\text{MnO}$	0.002-0.05	0.05-0.3	0.002-0.05
$\text{Na}_2\text{O}$	0.05-0.6	0.1-0.3	0.1-0.8
$\text{K}_2\text{O}$	0.05-0.5	0.2-0.7	0.2-0.6
$\text{SO}_3$	0.2-1.5	0.6-2.7	0.3-3.1
$\text{TiO}_2$	0.03-0.08	0.05-0.2	0.05-0.1
$\text{BaO}$	Trace	0.01-0.03	0.07
$\text{CuO}$	0.0005-0.003	0.002-0.003	0.003-0.01
$\text{NiO}$	0.003	0.0005	—
$\text{ZnO}$	0.0005	0.001	0.001-0.025
$\text{SnO}_2$	0.002	0.001	—
$\text{MoO}_3$	0.002	0.002	—
$\text{V}_2\text{O}_5$	Trace-0.02	—	0.05-0.4
$\text{Cr}_2\text{O}_3$	Trace-0.015	0.003-0.007	0.05-0.15
$\text{B}_2\text{O}_3$	0.002-0.01	0.003-0.007	0.002-0.007
$\text{As}_2\text{O}_3$	0.001-0.005	0.002-0.004	0.001-0.015
Se	Trace	Trace	Trace-0.006
$\text{CO}_2$	1.5-4.4	1.0-2.0	0.7-4.2
Organic carbon	0.25-0.4	0.005-0.025	0.7-2.7
N	0.005-0.02	0.005-0.025	0.01-0.1

On exposure to fluorine in water, replacement took place leading to considerable amounts of the much less soluble fluorapatite,  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  or  $[\text{Ca}_3(\text{PO}_4)_2]_3 \cdot \text{CaF}_2$ . However, most phosphates produced in the U.S. contain from about 20 to 35% more fluorine than is theoretically necessary for the formation of fluorapatite; the remaining fluorine is present as calcium fluoride. In laboratory tests where fluorapatite was

precipitated from solution, the precipitate never contained more than 73% fluorapatite. The rest was the hydroxylapatite. When phosphate rock is defluorinated at 2750, 2800, and 2900°F., the defluorination takes place in two stages. The first is considered to be that of calcium fluoride. The fluorine content is lowered to about 70% of that required to form fluorapatite. From very finely ground phosphate rock, about 25–30% of the total phosphate can be extracted with ammonium citrate solution. The fluorine in excess of the amount needed to have about 70% of the total phosphate in form of fluorapatite probably exists as calcium fluoride.

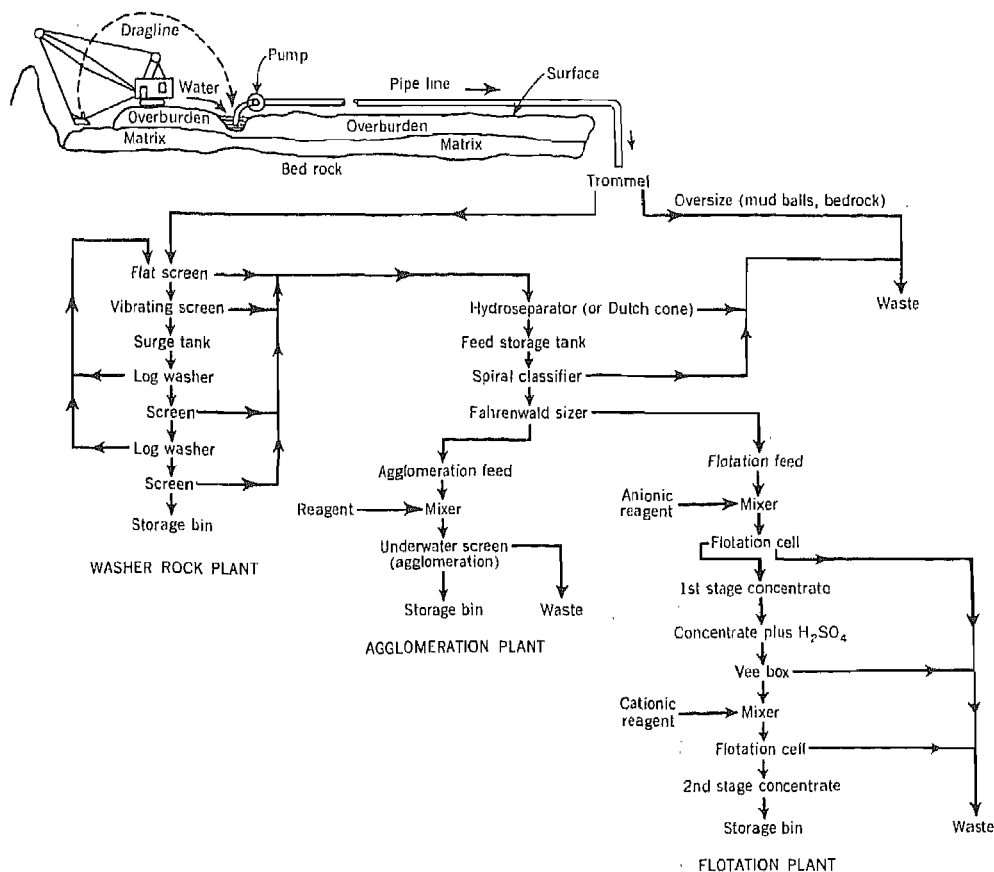


Fig. 5. Mining operation of Florida land-pebble phosphate rock.

Experimental evidence indicates that most of the carbonate exists as calcium carbonate and only a very minor quantity seems to exist as carbonate-apatite.

**Florida Land-Pebble Phosphates.** The principal phosphates in Florida are land-pebble phosphate and hard-rock phosphate. The land-pebble phosphate deposits are by far the most important in Florida and, from the standpoint of production, they have been the most important in the U.S. since 1905.

Pebble phosphate is mined in open pits. The overburden, ranging from 5 to about 30 ft. in thickness and consisting of sandy soil, hard pan, silt, and clay is removed by electrically operated draglines of the "walking type" with capacities up to 1500 tons per hour. See Figure 5.

After the overburden has been removed, the underlying matrix containing the phosphate pebbles and fines, which are embedded in clay and sand, is raised to the surface with a dragline. The matrix ranges in thickness from about 6 to 25 ft. At the surface it is dumped into a depression made by the dragline. Streams of high-pressure water disintegrate the matrix into a slurry containing 20-30% solids which is pumped in 12-16 in. pipe lines to a washer and recovery plant.

*Washer Rock:*  $\frac{1}{16}$  to 1 in. Particles coarser than about  $\frac{1}{16}$  in., called washer rock, comprise anywhere from 15 to 85% of the phosphate of a mine, depending on the nature of the deposit. They are separated from the rest of the slurry by a series of vibrating screens equipped with water sprays. Mud balls, clay, and other foreign matter adhering to the washer rock are removed by log washers and water sprays in the wet-screening operation. The coarser phosphate pebbles are usually separated from the smaller by screening because the coarser pebbles tend to be lower in phosphoric acid content.

*Flotation Concentrates:* -48 to +150 Mesh. Phosphate and sand particles less than about  $\frac{1}{16}$  in. down to +150 mesh are freed from clay and nearly colloidal calcium, iron, and aluminum phosphates by means of hydroseparators or Dutch cones. The phosphate and sand settle to the bottom, from which they are continuously removed and are subjected to additional washing and sizing with rakes, spirals, and Fahrenwald sizers. The washed product of about -16 to +150 mesh is usually sized, the major fraction of about -48 to +150 mesh going to the flotation plant and the -16 to +48 mesh fraction going to the agglomeration or tabling plant.

The wet flotation feed is mixed with fatty acids, sodium hydroxide, and fuel oil. Slight adjustments in the amount of reagents added have to be made frequently as the feed changes in physical and chemical properties. In the flotation cells the oil-coated phosphate particles attach themselves to the air bubbles and rise to the surface where they are skimmed off. The uncoated sand is discharged continuously at the bottom. Table XI gives an example of flotation results.

TABLE XI. One-Stage Flotation.

Reagents per ton of feed:	
Sodium hydroxide.....	0.30 lb.
Fatty acid (tall oil).....	0.43 lb.
Fuel oil.....	1.29 lb.
Recovery data:	
pH of water in flotation cell.....	8.50
P <sub>2</sub> O <sub>5</sub> in feed.....	14.20%
P <sub>2</sub> O <sub>5</sub> in recovered phosphate.....	33.70%
Silica in recovered phosphate.....	5.62%
P <sub>2</sub> O <sub>5</sub> in waste product.....	3.49%
P <sub>2</sub> O <sub>5</sub> recovery from feed.....	92.12%

TABLE XII. Two-Stage Flotation.

Reagents per ton of feed:	
First stage	
Sodium hydroxide.....	0.30 lb.
Fatty acids.....	0.43 lb.
Fuel oil.....	1.22 lb.
Second stage	
Sulfuric acid.....	3.00 lb.
Cationic reagent (amine).....	0.16 lb.
Sodium hydroxide.....	0.20 lb.
Frother (pine oil).....	0.16 lb.
Recovery data	
P <sub>2</sub> O <sub>5</sub> in feed.....	18.30%
P <sub>2</sub> O <sub>5</sub> in recovered phosphate.....	36.05%
Silica in recovered phosphate.....	3.21%
P <sub>2</sub> O <sub>5</sub> in waste product.....	7.49%
P <sub>2</sub> O <sub>5</sub> recovery from feed.....	94.30%

An alternate method, which requires fewer cells, less supervision, and less frequent adjustment in reagent measurement is two-stage flotation. A heavy load is put through the flotation cells which results in a less concentrated phosphate in the first stage. The product is then subjected to a second flotation step where it is first treated with dilute sulfuric acid, which removes most of the chemicals with which the phosphate particles are coated. The material is then washed to remove the oil slimes which rise to the surface. To the deslimed product are added amines of higher fatty acids such as the Arneens. Rosin-derived amines and quaternary ammonium compounds may also be used. (See *Flotation*.) These amines are used in a slightly alkaline medium in the presence of some frothing reagent such as pine oil, or some of the five or six carbon iso-alcohols. These reagents now coat the sand particles, so that in the flotation cell, the sand floats to the surface and the phosphates are continuously discharged at the bottom. Table XII gives an example of two-stage flotation.

*Agglomeration: -16 to +48 Mesh.* The coarser fraction of phosphate feed ranging from -16 to +48 mesh is too heavy for efficient recovery by flotation. It may be treated with a mixture of fatty acids, sodium hydroxide, and fuel oil similar in quantity to that used in flotation. The reagents again coat the phosphate particles which tend to agglomerate under water. If the selectively oiled feed is put on a 16-20 mesh inclined underwater screen (about 50°), the larger agglomerated phosphate particles roll down the screen while the sand goes through the screen meshes. Efficient separation of sand from phosphate of coarse feed is obtained by this simple process on Wilfley shaker tables. Humphrey spiral classifiers may also be used for recovery of the coarse selectively oiled phosphate fraction from coarse sand. See also *Flotation*; *Gravity concentration*; *Size separation*.

**Tennessee Phosphate Deposits.** Although three types of phosphate rock—brown, blue, and white—occur in Tennessee, only the brown rock phosphate is commercially important at present. The brown rock deposits are located near Nashville, Mount Pulaski, and Gallatin in central and south central Tennessee.

The brown rock, locally called "matrix" or "muck," consists of pebble plate, lump, and honey-combed textured rock, along with soft and hard clay masses and phosphatic sand containing 20-30% moisture. The amount of overburden is usually very light and ranges from nothing up to 20 ft. The matrix has a depth of a few inches up to about 15 ft. At the bottom of the matrix is limestone. There are "cutters" or "drainage channels" in the limestone, varying in width from 1 up to 30 ft. or more. They are usually filled with high-grade rock and phosphatic sand. The overburden is removed with draglines and the matrix is loaded on trucks which haul it to a washer.

At first the mining in Tennessee was designed to produce only lump phosphate rock, grading about 34-35%  $P_2O_5$ . A little later, phosphate approaching sand in particle size was mined. This brought about the mining of the most desirable deposits until higher analyses were no longer available. Now grades mined for making superphosphate range from 31 to 35%  $P_2O_5$ ; ground rock for direct application to the soil is about 30%  $P_2O_5$ ; and material 23%  $P_2O_5$  and up is used for electric-furnace production of elemental phosphorus.

Strip mining is used by all the companies. The matrix hauled by trucks is dumped into soaking pits where the water aids in breaking up the clay that is associated with most of the matrix. The matrix is pumped to washing plants and there with the aid of grizzlies, scrubbers, screens, hydroseparators, and rakes, clay and low-analysis phosphate material is separated from the rock.

Frequently three products are produced consisting of -22 to +100 mesh, -100 to +200 mesh, and unground material coarser than 22 mesh. In case it is desired to produce furnace-grade rock only, there is less crushing of the pebble material and less rewashing and classification of the higher grade. Emphasis is put on higher recovery rather than higher grade.

Some miners subject the -100 mesh to +175 mesh screen fraction to flotation in order to raise the grade.

**Western Phosphate Deposits.** The most extensive, known phosphate deposits in the world are in the states of Idaho, Utah, Montana, and Wyoming. They contain large tonnages of high-grade rock suitable for making ordinary and triple superphosphate by the wet process. There are also vast quantities of rock of lower phosphate content which can be manufactured into concentrated products by means of the electric or blast furnace (65).

Due to inaccessibility of many deposits, high cost of transportation to large established markets, inadequately developed local sources of electric energy and heavy chemicals, and limited local demand for fertilizer, extensive western phosphate mining has been delayed. However, new improved highways, additional railroad facilities, new sources of electric energy, and new technological developments will favor increased mining activity.



Since large fertilizer consuming areas are as much as 800 to 1600 miles from the phosphate deposits, it is logical that the phosphate rock be converted into more concentrated products near the source of raw material. Manufacture of triple superphosphate by the wet process is a logical development since cheap sulfuric acid obtainable from roasted pyrite ores is available in large amounts. For production of relatively pure phosphoric acid, the electric- or blast-furnace process is preferable.

The currently economic phosphate-bearing formation is of marine origin and consists of yellowish-brown phosphatic sandstones, dark brown to black phosphatic shales, and brown to black limestone. The richest bed of phosphate rock is 4–7 ft. thick over large areas and the phosphoric acid content ranges from 26 to 37%. Both underground and open pit mining are practiced. Some of the open pit mines now being worked contain 60–75 ft. of overburden. Most western deposits have to be mined selectively in order to avoid mixing low-grade rock with material of higher analysis. Beneficiation by washing and flotation is not practical at some mines because of lack of water.

### Superphosphate

Superphosphate is made by acidulating phosphate rock with sulfuric acid. It consists approximately of 30% monocalcium phosphate,  $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ; 10% dicalcium phosphate,  $\text{CaHPO}_4$ ; 45% calcium sulfate,  $\text{CaSO}_4$ ; 10% iron, aluminum oxides, silica, etc.; and 5% moisture. Superphosphate is the chief material supplying phosphoric acid in fertilizers and may be considered the basis of the modern fertilizer industry. It usually contains 18–21% available  $\text{P}_2\text{O}_5$ .

Production of superphosphate since 1880 in the U.S. according to the National Fertilizer Association is shown in Table XIII. Estimated world production of superphosphate for 1938 and 1947 is shown in Table XIV.

TABLE XIII. Production of Superphosphate in the U.S.

Year	Production, tons	Year	Production, tons
1880.....	205,000	1940.....	4,865,000
1900.....	1,505,000	1945.....	8,039,000
1920.....	5,130,000	1947.....	10,315,000
1930.....	4,415,000	1948.....	10,553,000

Early attempts at making superphosphate were crude. Bone dust was sprayed with sulfuric acid in open boxes. The mixture was raked back and forth and allowed to react until it was sufficiently solidified to be stored in sheds for further curing.

As time went on the supply of bones became inadequate to meet the demand and new sources of raw phosphate had to be used. Some of the phosphates were much harder and they had to be ground much finer for making superphosphate.

Better mills were developed for grinding the phosphate rock to a higher degree of fineness. The most widely used mills in the U.S. and many foreign countries for pulverizing phosphate rock are the Raymond roller mills manufactured by the Raymond Pulverizer Division of Combustion-Engineering-Superheater, Inc., Chicago, Illinois (see *Size reduction*).

The grinding action in these mills consists of heavy rollers traveling around the inside surface of a stationary grinding ring. These mills are equipped with internal air separation. Only material which has been reduced to the required particle size can be carried out of the mill to the finished-product collecting equipment. There is no external recirculation of material. Simultaneous drying and grinding is used to good advantage when the initial moisture is comparatively low. The entire vertical shaft assembly, including the spider which carries the journals and grinding rollers, as well

TABLE XIV. World Production of Superphosphate, Long Tons.

Location	Year	
	1938	1947
<b>Europe</b>		
Austria.....	44,000	670
Belgium.....	273,600	612,785
Czechoslovakia.....	128,213	203,105
Denmark.....	366,414	374,998
Eire.....	559,930	120,002
Finland.....	22	57,687
France.....	1,172,681	1,429,202
Germany.....	1,100,000	350,000
Great Britain.....	—	981,774
Greece.....	67,917	72,910
Holland.....	569,850	752,486
Hungary.....	43,900	16,000
Italy.....	1,405,862	1,035,113
Norway.....	31,040	25,864
Poland.....	227,869	182,976
Portugal.....	226,500	297,408
Rumania.....	15,187	—
Spain.....	320,000	365,050
Sweden.....	260,398	305,470
Switzerland.....	16,571	26,630
U.S.S.R.....	1,878,780	2,000,000
Yugoslavia.....	19,756	40,000
<i>Total Europe.....</i>	<i>8,728,790</i>	<i>9,250,130</i>
<b>Africa</b>		
Egypt.....	20,450	22,055
North Africa.....	156,986	192,500
South Africa.....	142,476	293,023
<i>Total Africa.....</i>	<i>319,912</i>	<i>507,578</i>
<b>America</b>		
Brazil.....	—	40,570
Canada.....	89,940	232,596
Uruguay.....	2,837	600
U.S.....	3,644,600	9,357,352
<i>Total America.....</i>	<i>3,737,377</i>	<i>9,631,118</i>
<b>Asia</b>		
India.....	—	10,000
Japan.....	1,630,000	705,000
Palestine.....	—	3,300
Turkey.....	—	4,447
<i>Total Asia.....</i>	<i>1,630,000</i>	<i>722,747</i>
<b>Oceania</b>		
Australia.....	1,263,943	1,127,506
New Zealand.....	964,389	562,683
<i>Total Oceania.....</i>	<i>2,228,332</i>	<i>1,690,189</i>
<i>Total world production.....</i>	<i>16,644,411</i>	<i>21,801,762</i>
<i>Average grade, %.....</i>	<i>17.22</i>	<i>17.6</i>

Source: International Superphosphate Manufacturers Association, London.

as the plow support and plows, revolves. Most of the feed as it enters the mill through the automatic feeder falls to the mill bottom. A plow just ahead of each roller scoops up material from the mill bottom, throwing it to just the proper location so that the roller will catch it against the grinding ring. The base of the mill is surrounded by an air housing. Comparatively large quantities of air enter the bottom of the mill below the rollers through tangential ports, and carry the finer materials into the classifying zone. In a whizzer-equipped mill, the centrifugal action of revolving whizzer blades concentrates the larger particles along the outside of the mill. These again work back down into the grinding zone for further reduction. Only material which has been reduced to the proper size reaches the outlet at the top of the mill, and is carried on to the finished-product collecting equipment. The whizzer separator is always operated by a variable-speed device. Fineness control is simply a matter of whizzer speed.

Maximum capacity and uniformity of product are obtained by automatic feed-control equipment. The controller governs the feed roll, depending upon the pressure drop across the mill. This is possible because there is a relationship between quantity of material in the mill and the pressure drop across the mill.

Both whizzer-equipped high-side Raymond roller mills and also low-side Raymond roller mills are used for phosphate rock grinding. The whizzer-equipped mills can produce a complete range of fineness from 50% through 200 mesh up to 95% or more through 200 mesh. A feature of the whizzer-equipped mills is ease of fineness regulation and uniformity of results. Low-side Raymond roller mills are equipped with single-cone separators. The best applications for these mills are jobs where only one fineness of grind is required and the usual limit of fineness for the low-side unit is about 95% through 100 mesh.

The Raymond roller mills are available in a range of sizes for capacities from about 4 tons per hour to 30 tons per hour or more, depending upon fineness of grind and source of rock.

The approximate particle-size distribution when grinding either Florida or Tennessee phosphate rock, 90% through 100 mesh, is as follows:

Through mesh.....	40	50	60	70	80	100	200
Cumulative, %.....	99.9	99.5	98.7	97	94	90	70

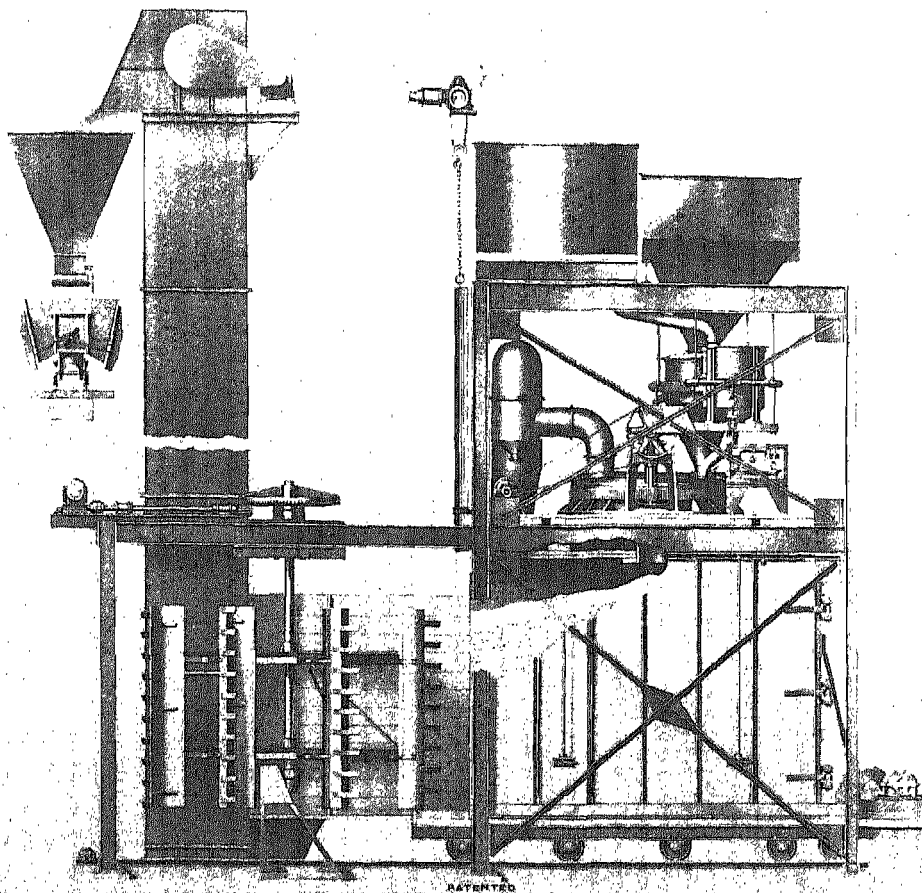
About 1880, when Florida phosphate rock began to be used, it became necessary to confine the reacting mixture of phosphate rock and sulfuric acid to closed chambers, in order to absorb the objectionable gases liberated in towers containing water sprays. Mechanical means of mixing the phosphate and sulfuric acid in vertical cylinders with a mixing shaft replaced hand mixing.

**Dens.** The receptacle in which the freshly acidulated superphosphate was placed was known as the den. After the mixture of finely ground rock and sulfuric acid had solidified, it was removed manually with forks from the dens or chambers into hand carts and placed in the storage pile for additional curing. In the U.S. this method is rarely used today.

In the excavation of dens, various mechanical devices such as shovels, crane buckets, draglines, and revolving cutters began to replace hand labor since about 1900. A number of different mechanically excavated dens are now in use in the U.S.

When crane-type plants were erected and most of the moving of materials was done by electrically operated cranes, the crane was also utilized for excavating the superphosphate dens.

In several large as well as smaller establishments, superphosphate is still made in steel-reinforced concrete dens of 100–300 tons capacity, which are excavated by drag-lines or crane buckets. The dens are rectangular and are used in pairs. While one den is charged, the other is being discharged. The dens are separated by a common wall. The two dens have one movable top, traveling on two steel rails, on which are mounted a batch mixer of one- or two-ton capacity and a phosphate rock hopper with a scale and sulfuric acid tank with a scale. The weighed rock and acid are discharged into the batch mixer.



*Courtesy Sturtevant Mill Company.*

Fig. 6. Sturtevant-Beskow den.

The acid rock slurry produced in the vertical shaft batch mixer is usually agitated from 25 to 50 seconds. The slurry is discharged into the den while still in a relatively fluid condition. The amount mixed ranges from about 25 to 60 tons per hour.

Both the mixer and the den being charged are provided with ducts for the removal of vapors containing fluorine compounds, carbon dioxide, and steam, which are liberated during the acidulation of phosphate rock. By means of fans, the gases may be drawn into scrubbers provided with water sprays or they may be removed by water ejectors. Most of the steam is condensed and the fluorine compounds are absorbed.

As the concentration of the acid used for acidulation and its temperature are increased, the amount of fluorine gases liberated increases. The fluorine content of superphosphate made from Florida pebble varies from about 1.2 to 2.0%. On the average only about 25% of the fluorine in the phosphate rock is volatilized. Superphosphate made from Tennessee brown phosphate undergoes from about 25 to 35% volatilization of fluorine.

Ex-cenning of the freshly made superphosphate by means of crane buckets may start about 15 minutes after the last charge is made or it may not be excavated until the following day. This type of excavation by crane buckets has the objection that the scraping and squeezing action of the crane bucket has a deleterious effect on the physical condition of the superphosphate. The manner in which freshly made superphosphate is handled has an important influence on the final physical condition of the product. In order to overcome these objections, other means of excavating dens are now in use.

In 1921, the Sturtevant-Beskow den was introduced into the U.S. (see Fig. 6). This den is really a flat car on wheels, the car having a self-propelling mechanism; the floor of the car corresponds to the den chamber. The back end of the car, a concrete wall, is built on the car, conforming to one side of the den chamber. The supporting structure around the car provides the roof for sealing of the den chamber and also the support of the mixer. Two steel frames covered with wood are hung from the supporting structure, and when forced up against the sides of the car, they thus provide two of the sides of the car. The fourth side is provided by a slidable door, raised or lowered by an electric hoist, and therefore when all sides are in position a box is provided for a den on the car. The charges from the mixer are fed into this box, and after it is filled up to prescribed height, a solid block of superphosphate is made. A very short while after the last charge is in the block, it solidifies and, therefore, will not flow. The front door is raised by the electric hoist. The side doors are loosened away from the block and the self-propelling mechanism withdraws the block of superphosphate from its enclosure. As it travels forward it meets the revolving cutter arranged with arms to create a fan effect and projections on the arms to act as cutters. When revolving at high speed, it fans against the face of the block, and the cutters remove the superphosphate, cutting a very thin slice, about  $\frac{1}{8}$  in. This was the first development of fanning action to assist in blowing out the steamy vapor even in the smallest pockets. Heretofore the excavators had been principally used to remove the material as quickly as possible, and of course the revolutions of the cutter created a certain fan effect; but the higher speed of operation of the Sturtevant cutters, plus the increased effect of the fan, remove the moisture more thoroughly. The superphosphate thus shaved off is discharged into an elevator for overhead distribution.

The Sturtevant den is popular in the U.S. as indicated by the large number of installations made. While at present the charging of the den is a batch mixing operation, the manufacturer is also considering continuous mixing. The Sturtevant den is made in two sizes, one having a capacity of 20 and the other 10 tons per hour.

A continuous process for mixing, conveying, and excavating superphosphate from the den was independently but simultaneously developed by M. Broadfield and by H. B. Siems (see Fig. 7). Instead of batchwise mixing of acid and phosphate rock, the mixing operation is a continuous one. The raw materials are continuously charged into a type of pug mill in which the slurry of rock and acid remain from 2 to 3 minutes. As long as this mixture is vigorously agitated, it does not solidify. The longer reten-

tion time in the pug-mill mixer permits more intimate mixing, and it produces a final product which is somewhat denser and more granular than most superphosphate made by other means.

The slurry is discharged onto a continuous slat conveyor. The slat conveyor forms the bottom of the den. Originally the side walls moved continuously with the same speed as the slat conveyor. However, Siems found that the moving side walls can be replaced with stationary walls provided the freshly discharged superphosphate slurry from the pug-mill mixer enters a preforming chamber. The moving slat conveyor is the bottom of this chamber and the stationary side walls are a little closer together where the slurry drops on the conveyor. The side walls gradually widen for about 8 ft. Before the fresh superphosphate has traveled that far it has set into a block which remains about 2 in. distant from the remaining stationary side wall. At the discharge end of the slat conveyor, the superphosphate is removed by revolving cutters or cutter blades on an endless chain.

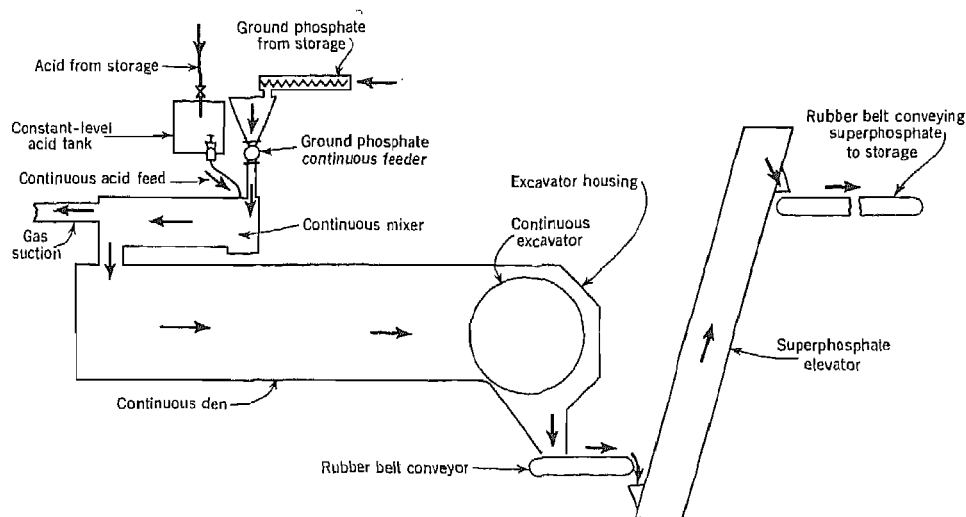


Fig. 7. The Broadfield process (45).

On the original Broadfield den, the superphosphate remained on the moving den conveyor for about two hours. However, Siems found that with proper acid strength and temperature control, the freshly made superphosphate need only remain on the conveying den 8-30 minutes before it is discharged.

In the proper proportioning of phosphate rock and sulfuric acid, no difficulty is experienced in obtaining a uniform and predetermined amount of flow of acid. It may be done with a constant-level box with a suitable orifice plate made of a glass tube in the discharge pipe. Another alternative is a siphon which provides a constant head of acid by being attached to two hollow lead floats. The siphon moves up and down with the floats as the level of the acid changes. In order to vary the rate of flow of acid, the siphon is either raised or lowered with respect to the lead floats. Continuous flow of a predetermined amount of phosphate rock presents more of a problem. Continuous volumetric feeding of rock is not satisfactory because of variation of weight of ground rock per given volume depending principally on the time interval since grinding and the amount of aeration in handling. The weight of freshly ground rock may be as much as

20% less by weight per unit volume than rock ground one hour earlier. Gravimetric devices for controlling and measuring the continuous flow of phosphate rock are therefore preferable. Devices such as the poidometer, modified for handling of phosphate rock, or the gravimetric Synttron, are in use. Proper control of flow of phosphate rock with these devices depends on the skill and experience of the operator.

The Kuhlmann superphosphate process was developed and is operated in France for making superphosphate by a continuous process. So far no installation has been made in the U.S. The American Industrial Development Corporation has the American rights to the process.

Ground phosphate rock is fed through the rock bin to a constant-weight feeder. It then drops onto a small mixer, similar to the mixer developed by the TVA, where it is mixed for a few seconds with sulfuric acid. The feeding of both phosphate rock and acid is continuous. While the mixture is still fluid it drops onto a 75-ft. rubber conveyor belt, where it sets rapidly. This belt is troughed for approximately 45 ft., and then widens out to a flat belt, where the already caked mass cracks open, permitting further escape of the vapors. At the end of the belt, it is brushed off by a squirrel-cage disintegrator. After this the mass is conveyed either to storage piles or to the shipping department. The owners of the process claim for it less capital investment per ton of superphosphate than for the batch process.

There is good reason to believe that other and still better continuous processes will be developed for making better superphosphate, if factors such as acid temperature and concentration, fineness of grinding of phosphate rock, proper proportioning of rock and acid, time and intensity of mixing phosphate rock and acid slurry, and duration of freshly made product on the belt conveyor before disintegrating are controlled within desirable limits.

**Acidulation of Phosphate Rock.** While it is now common practice to acidulate phosphate rock with 53–57°Bé. sulfuric acid, the use of higher-strength acid is preferable, provided that a superphosphate with good physical and chemical properties is obtained. In order to accomplish this it will be necessary to determine how various factors just mentioned must be controlled. Instead of one-step acidulation, two or more steps may have added advantages, particularly with higher-strength sulfuric acid.

Producers of superphosphate usually try to proportion the phosphate rock and sulfuric acid so that there is neither a surplus of acid nor of unreacted phosphate rock. There are, however, conditions which make it desirable to alter the phosphate rock – acid ratio. When the time for curing is short, it may be desirable to increase the amount of sulfuric acid used, in order to hasten the rate of decomposition of the phosphate rock. If considerable time is available, the amount of sulfuric acid used may be decreased. However, if the resultant product is to be used in mixed fertilizers and is to be treated with ammoniating solutions, the use of reduced quantities of acid is usually not advisable.

Various schemes for estimating the amount of acid required for acidulating phosphate rock have been proposed. One method is to calculate the sulfuric acid that will be required to change the oxides of calcium, aluminum, iron, magnesium, sodium, potassium, manganese, and other basic reacting elements of phosphate rock into sulfate. Since, however, the basic elements in phosphate rock are not present in form of oxides but as phosphates, sulfates, and fluorides, less acid will be required than would be the case if all the base-forming elements were present in the form of oxides. There-

fore, dependent on the amount of  $P_2O_5$ ,  $SO_3$ , and fluorine present, a correction factor must be applied. (No correction need be made for carbonates since their acid requirement is the same as the oxides.)

Table XV (35) shows the composition and acid requirement of six samples of

TABLE XV. Composition of Florida Pebble Rock and Sulfuric Acid Weight Factor.

Constituent	Range in compn., %	Av. compn., %	Sulfuric acid (100%), lb./lb. metal oxide
CaO	47.20-49.77	48.32	1.748
Al <sub>2</sub> O <sub>3</sub>	0.81-1.05	0.95	0.962
Fe <sub>2</sub> O <sub>3</sub>	0.68-1.90	1.23	0.614
MgO	0.04-0.21	0.14	2.430
Na <sub>2</sub> O	0.07-0.60	0.40	1.581
K <sub>2</sub> O	0.09-0.25	0.16	1.041
MnO	0.005-0.050	0.015	1.382
P <sub>2</sub> O <sub>5</sub>	31.28-35.55	33.78	-0.690
SO <sub>3</sub>	0.20-2.10	1.17	-1.224
Fluorine	3.87-4.04	3.95	-1.550 <sup>a</sup>

<sup>a</sup> Assuming volatilization of  $33\frac{1}{3}\%$  fluorine, the acid weight factor becomes -0.517.

Florida land-pebble phosphate. In the last column is shown the amount of 100% sulfuric acid required per pound of metal oxide and the amount that may be deducted (as shown by the negative sign) for each pound of  $P_2O_5$ ,  $SO_3$ , and fluorine.

Iron and aluminum oxides are usually reported as combined total iron and aluminum oxides, and since the total is relatively small, the average sulfuric acid requirements may be used. Since the acid requirements for the oxides of magnesium, sodium, potassium, manganese in phosphate rock are not greatly different and since only relatively small amounts are present, the average acid requirements for all may be taken in this instance.

The analysis of a Florida land-pebble rock and the amount of sulfuric acid necessary for acidulation of 100 lb. is shown in Table XVI.

TABLE XVI. Analysis of Florida Land-Pebble Rock and Sulfuric Acid Required for Acidulation.

Constituent	Amount, %	Sulfuric acid, lb./100 lb. phosphate rock <sup>a</sup>
CaO.....	48	83.90
Al <sub>2</sub> O <sub>3</sub> and Fe <sub>2</sub> O <sub>3</sub> .....	2.50	1.97
MgO, Na <sub>2</sub> O, K <sub>2</sub> O, and MnO.....	0.72	1.16
Total P <sub>2</sub> O <sub>5</sub> .....	33.70	-23.25
Total SO <sub>3</sub> .....	0.17	-1.32
Total fluorine.....	3.95	—
Fluorine liberated (33 $\frac{1}{3}$ %).....	1.32	-2.05
		60.41

<sup>a</sup> Using acid weight factors given in Table XV.

According to Table XVI, 60.41 lb. of 100% sulfuric acid or 86.7 lb. of 55°Bé. sulfuric acid will be required per 100 lb. of phosphate rock. This is the theoretical value for 100% acidulation of a given Florida phosphate rock. A survey revealed that eight large producers of superphosphate use quantities of acid ranging from 89 to 111% of the theoretical amount required (35). The acid strength ranged from 55 to 56°Bé.

Most manufacturers change the phosphate rock - sulfuric acid ratio only if the



chemical analysis of the superphosphate shows either too little or too much sulfuric acid as indicated by the amount of insoluble  $P_2O_5$  or the free phosphoric acid ( $H_3PO_4$ ) content. If insufficient acid is used, the superphosphate, after adequate cure, will contain about 3%  $H_3PO_4$  and an excess of about 0.4% insoluble  $P_2O_5$ . On the other hand, if in a cured product the insoluble  $P_2O_5$  content is about 0.3% or less, and if the free  $H_3PO_4$  obtained by extraction with acetone or 95% alcohol is more than 3-4%, excess sulfuric acid was used in the acidulating formula.

Well-cured and properly made superphosphate contains about 3% free  $H_3PO_4$ . Each 1%  $H_3PO_4$  above 3% will make "available" about 0.33%  $P_2O_5$  of the unreacted phosphate rock in superphosphate. Thus superphosphate with 9% free  $H_3PO_4$  and 2.75% insoluble  $P_2O_5$ , after adequate curing, can be expected to show about 3% free  $H_3PO_4$  and 0.75% ammonium citrate-insoluble  $P_2O_5$ . If the fresh superphosphates show 9% free  $H_3PO_4$  and 3.75% insoluble  $P_2O_5$ , the product when cured will analyze about 3% free  $H_3PO_4$  and 1.75% insoluble  $P_2O_5$ . In this instance, too little acid was used for acidulation of phosphate rock.

In order to reduce the insoluble  $P_2O_5$  content by 1%, 3% additional free phosphoric acid would be required in the superphosphate. This is equivalent to adding 30 lb. of 100% sulfuric acid to the acidulating formula. Similarly, if the superphosphate contained 6% free  $H_3PO_4$ , and the insoluble  $P_2O_5$  content was about 0.2%, the product would contain about 3% more free phosphoric acid than needed and the sulfuric acid used in acidulating could be decreased by 30 lb. for each 3% surplus phosphoric acid in the superphosphate.

TABLE XVII. Change in the Analysis of Superphosphate with Age.

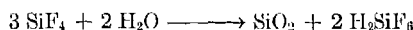
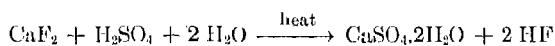
Age, days	Temp., °F.	Available $P_2O_5$ , %	Insol. $P_2O_5$ , %	Total $P_2O_5$ , %	Free $H_3PO_4$ , %
As made	224	17.09	2.51	19.60	10.97
1	158	18.38	1.43	19.80	7.85
2	156	18.74	1.24	19.98	8.22
3	156	18.84	1.14	19.98	7.91
4	156	18.95	0.95	19.90	6.49
7	160	19.13	0.85	19.98	5.88
8	158	19.17	0.75	19.92	5.64
9	156	19.18	0.70	19.88	5.39
11	146	19.42	0.70	20.12	4.90
14	139	19.37	0.65	20.02	5.02
15	138	19.57	0.55	20.12	4.66
16	116	19.45	0.55	20.00	4.53
19	122	19.65	0.45	20.10	4.41
20	118	19.61	0.37	19.98	4.41
21	117	19.65	0.45	20.10	4.17
23	114	19.68	0.40	20.08	3.92
30	109	19.95	0.37	20.32	3.43
36	112	19.85	0.25	20.10	3.31
44	92	20.12	0.28	20.40	3.06
51	94	20.17	0.33	20.50	3.06
58	92	20.19	0.25	20.44	2.94

Fineness of grinding of the phosphate rock greatly influences the rate of decomposition of the acidulated phosphate rock. However, extremely fine grinding is not

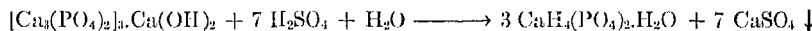
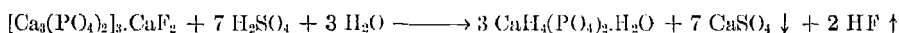
economical. Most of the Florida land-pebble phosphate rock is now ground so that from 85 to 95% will pass a 100-mesh Tyler screen.

Table XVII shows the change with age in the analysis of a sample of superphosphate. The sample was made by acidulating 1175 lb. of Florida land-pebble phosphate with 975 lb. of 56°Bé. sulfuric acid. The ground phosphate analyzed as follows: total  $P_2O_5$ , 33.60%;  $CaCO_3$ , 7.32%;  $Fe_2O_3$  and  $Al_2O_3$ , 2.16%;  $SiO_2$ , 7.91%; 89.1% passed 100 mesh. The original acid temperature was 110°F. and the ground phosphate temperature was 113°F.

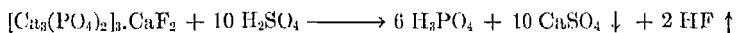
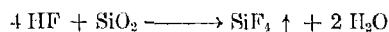
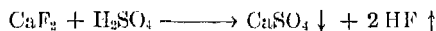
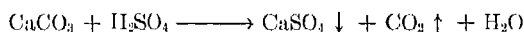
*Chemical Reactions.* Many writers still represent the chemical reactions occurring during acidulation as follows:



However, since the phosphate in the rock is mostly fluorapatite and hydroxylapatite, the principal reactions with 53–57°Bé. sulfuric acid are:



Other reactions are:



Iron and aluminum, magnesium, manganese, sodium, and potassium compounds in the phosphate rock are probably converted to the corresponding phosphates.

In the above equations, hydrogen fluoride is written HF, since it is a mixture of polymeric forms and cannot be represented by any one formula. The hydrogen fluoride liberated during acidulation attacks the silica in the phosphate rock and is liberated as silicon tetrafluoride at 215–235°F.

Calcium sulfate formed during acidulation of the phosphate rock with 53–57°Bé. sulfuric acid is not the dihydrate,  $CaSO_4 \cdot 2H_2O$ , but anhydrite,  $CaSO_4$ . The high temperature and high-strength phosphoric acid existing during acidulation do not favor the formation of  $CaSO_4 \cdot \frac{1}{2}H_2O$  and  $CaSO_4 \cdot 2H_2O$ . The hardening in superphosphate is due principally to the hydration of monocalcium phosphate,  $CaH_4(PO_4)_2$ , to  $CaH_4(PO_4)_2 \cdot H_2O$ .

The amount of fluorine compounds liberated in making cured superphosphate varies from about 20 to 34% of the total fluorine in Florida land pebble, from 28 to

36% in Tennessee, and from 33 to 38% in Idaho and Montana phosphate rock. Usually an increase in either sulfuric acid concentration or temperature or both, or longer and more vigorous agitation during the mixing operation, tends to increase the amount of fluorine compounds and steam liberated. The amount given off may vary from 6 to 11% of the weight of phosphate rock and acid used in the acidulating formula. The gases are usually scrubbed in spray towers or noxious vapor condensers to remove the fluorine compounds (see *Fluorine compounds*.)

Most of the fluosilicic acid,  $\text{H}_2\text{SiF}_6$ , produced goes to waste since the cost of recovering it in a more concentrated form or converting it into sodium fluosilicate (silicofluoride) frequently leaves no margin of profit. Some manufacturers, however, recover the fluorides as sodium, ammonium, magnesium, zinc, and copper salts. Sodium fluosilicate is the most common of the salts made.

### Wet-Process Phosphoric Acid

Since most of the phosphoric acid produced by the wet process is used in the manufacture of fertilizers, it is described here rather than under *Phosphoric acids*. In the wet process, phosphoric acid is made by leaching phosphate rock with sulfuric acid. This results in a relatively impure acid. It is not necessary that the resultant acid be purified for making either triple superphosphate or fertilizer ammonium phosphate. For most other purposes, however, it must be purified.

Wet-process phosphoric acid made from Utah phosphate rock, which was calcined to destroy the high organic-matter content, analyzed as shown in Table XVIII.

TABLE XVIII. Analysis of Wet-Process Phosphoric Acid from Utah Phosphate Rock.

Constituent <sup>a</sup>	Amount, %	Constituent <sup>a</sup>	Amount, %
$\text{P}_2\text{O}_5$ .....	53.50	$\text{TiO}_2$ .....	0.58
$\text{SO}_3$ .....	2.55	$\text{CaO}$ .....	0.25
$\text{Fe}_2\text{O}_3$ .....	1.00	V.....	0.24
$\text{Al}_2\text{O}_3$ .....	0.99	$\text{SiO}_2$ .....	0.14
F.....	0.77		

<sup>a</sup> The following elements were present in amounts less than 0.1%: Mg, As, Na, K, Cr, Cu, Mn, Pb, Zn, Ni, Ba, Sr, B, and Mo.  
Source: reference (31).

Crude phosphoric acid with about 53%  $\text{P}_2\text{O}_5$  content made from uncalcined Florida phosphate rock contains even more  $\text{CaO}$ ,  $\text{SO}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{SiO}_2$  than is shown in Table XVIII.

**History.** Wet-process phosphoric acid for manufacture of fertilizer materials was first made commercially in Germany in 1870. A low-grade ground domestic phosphorite which up to then had no commercial value was digested with 16% sulfuric acid in a batchwise process. The dilute phosphoric acid obtained contained about 8–10%  $\text{P}_2\text{O}_5$  and impurities consisting principally of calcium sulfate and iron and aluminum compounds. The dilute acid was pumped into concentrators where strong acid was formed by evaporation. The strong acid was used to make "double superphosphate" in a mixing pan in a process similar to that by which ordinary superphosphate was made with sulfuric acid at that time. By about 1900, there were 12 companies in Europe using the wet process on low-grade phosphate since there were no known high-grade deposits. After 1900, high-grade phosphate rock from the U.S. and other countries was sold relatively cheaply in Europe. It was used for making regular superphosphate which was sold for less per pound of available phosphoric acid than the double superphosphate, whose production therefore decreased. In the U.S., production of liquid phosphoric acid for fertilizer purposes began about 1890 in Baltimore, Maryland. The amount made was small.

The use of weak sulfuric acid (18%  $\text{H}_2\text{SO}_4$  or less) and the production of still weaker phosphoric acid was not a matter of choice but necessity, because the filters then available were not suitable for higher-strength phosphoric acid at an elevated temperature. About 1924, wet-process acid containing 22–23%  $\text{P}_2\text{O}_5$  was produced by decantation. The phosphate rock was subjected to wet grinding with sulfuric acid and weak phosphoric acid. The slurry and additional sulfuric acid and weak recycle phosphoric acid were sent to a series of agitators and thickeners. Plants and buildings based on the decantation principle are expensive and unwieldy. There are still several plants in the U.S. which use this or somewhat similar schemes.

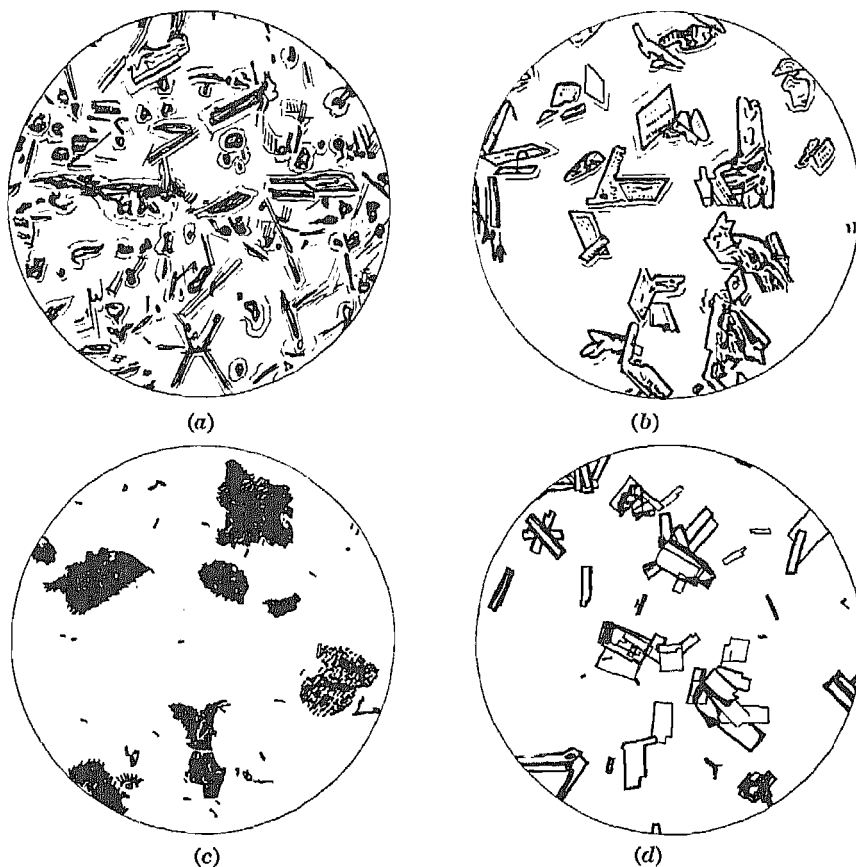


Fig. 8. Calcium sulfate crystals: (a) agglomerated hemihydrate; (b) stable anhydrite; (c) dihydrate crystals with low filtering speed; (d) dihydrate crystals with high filtering speed (44).

About the time the decantation principle was developed, a continuous mechanical vacuum filter suitable for acid containing 22–23%  $\text{P}_2\text{O}_5$  was developed by Oliver. In some plants the continuous filter has been substituted for the last or even the last three thickeners. The production of phosphoric acid containing 22–23%  $\text{P}_2\text{O}_5$  before evaporation marks a distinct advance over a product containing only about 12%  $\text{P}_2\text{O}_5$ . It is obvious that the production of a still stronger phosphoric acid in the leaching process is highly desirable because it will require less subsequent evaporation of the acid or drying of the product made with the acid.

During the period of 1926 to 1936, Sven Nordengren and his associates in Landskrona, Sweden, set out to make a strong phosphoric acid that would not require evaporation of the production acid. It was to be mixed with sulfuric acid in order to raise the grade of superphosphate made from low-grade phosphate rock. In 1926, little was known about how to make a good filterable sludge containing relatively strong acid, and what would make a suitable filter. In studying filterable sludge of concentrated mother liquor, it was found that the filtering conditions of sludge depended principally on

the form of calcium sulfate crystals, which occur in three forms: anhydrite,  $\text{CaSO}_4$ ; hemihydrate,  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ; and dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (see Vol. 2, pp. 767-79). Nordengren and associates found that the type of crystals produced depended on the temperature of the sludge and strength of phosphoric acid at the time of precipitation and the duration of the process. Stable crystals could be found in all crystal forms, but if the conditions were in the border regions between one form of crystal and another, sufficient unstable crystals were formed which eventually recrystallized on the filter making the cake impenetrable to the wash liquid. The main results of the research showed that the wet phosphoric acid process could be performed according to three different methods, characterized by the form of calcium sulfate left in the sludge, namely: (1) the dihydrate process; (2) the hemihydrate process; and (3) the anhydrite process.

Nordengren knew in 1926 of van't Hoff's work regarding the conditions under which various crystals of calcium sulfate were formed in water. The anhydrite exists as the common insoluble anhydrite that will not take up water, and the "soluble" anhydrite that will take up water readily. Nordengren found in 1928 that hemihydrate in phosphoric acid could be made into two different forms: one taking up water forming the dihydrate and the other being stable. The stable product could be washed on a filter, but the unstable product would take up water and form a solid cake of dihydrate, impenetrable to the washing solution.

Nordengren found that hemihydrate could be made in two crystalline forms. The stable hemihydrate crystals were small but agglomerated readily and the slurry could be easily filtered. Crystals

of this quality are shown in Figure 8(a). The unstable hemihydrate took up water and formed a solid cake impenetrable to wash solutions. The dihydrate crystals shown in Figure 8(c) have a low filter speed and those in Figure 8(d) a high one.

In order to produce easily filterable sludge, the reaction should be conducted in such a way that the calcium sulfate will form both stable crystals and large crystals (or agglomerate crystals). The forming of stable crystals with different amounts of water of crystallization depends mainly on the concentration of phosphoric acid in the sludge and the reaction temperature. Results of studies are shown in Figure 9. Dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , is formed below

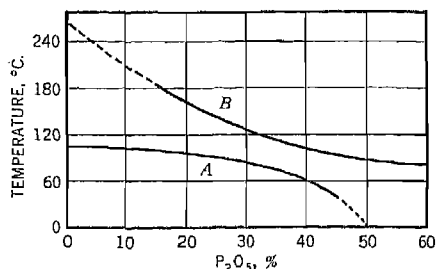


Fig. 9. Crystallization ranges of calcium sulfate hydrates (44).

curve A. In the area between curves A and B, unstable hemihydrate is formed. Immediately above curve B a stable hemihydrate may be produced. The corresponding curve of stable anhydrite has not been determined, but should be drawn almost parallel with curve B, although 15-20°C. higher.

**The Dihydrate Process.** Most of the phosphoric acid produced by the wet process has been manufactured under conditions which cause the formation of the dihydrate. Good filterable crystals of hemihydrate or anhydrite in a sludge containing less than 35%  $\text{P}_2\text{O}_5$  would require temperatures well above 100°C. and the reaction would have to be carried out in a closed vessel. Although the strength of the mother liquor in modern production acid ranges from about 28 to 33%  $\text{P}_2\text{O}_5$ , it is evident from Figure 9 that if the temperature of the reaction is kept sufficiently low, stable dihydrate crystals can be formed in sludges of still higher phosphoric acid concentration. A limit is imposed by the fact that it is difficult to obtain large and easily filterable crystals if the mother liquor exceeds 32%  $\text{P}_2\text{O}_5$ .

Formation of large-size crystals seems to depend on the amount of suspended solids in the sludge. In order to get good crystals, phosphoric acid should be recirculated in the process, whether the crystals are formed as dihydrate, hemihydrate, or anhydrite. If the strength of the circulating phosphoric acid is increased, the quantity circulating should also be increased. Increasing the amount of circulating phosphoric acid causes dilution of the  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions and also reduces the degree of supersaturation, which should favor formation of larger crystals. Increased viscosity can-

not be counteracted by increased temperature in the dihydrate process, because the temperature must be kept below curve 4 in Figure 9.

Nordengren gives an example of the dihydrate process as follows (see Fig. 10). Ground phosphate rock is mixed with circulating phosphoric acid containing 15–25%  $P_2O_5$ , and given time to react. Sulfuric acid is then added and in larger plants the sludge is cooled so that the limiting temperature will not be exceeded. The process is generally carried out continuously in 3 or 4 open digesters and the weighing of ground phosphate rock and measuring of acid is performed automatically. The time of reaction is considerable, ranging from 10 to 24 hours, but in spite of this, 4–6% of the total phosphoric acid content of the phosphate rock remains unreacted. Wash losses included, the average yield of the process will be 92–94%.

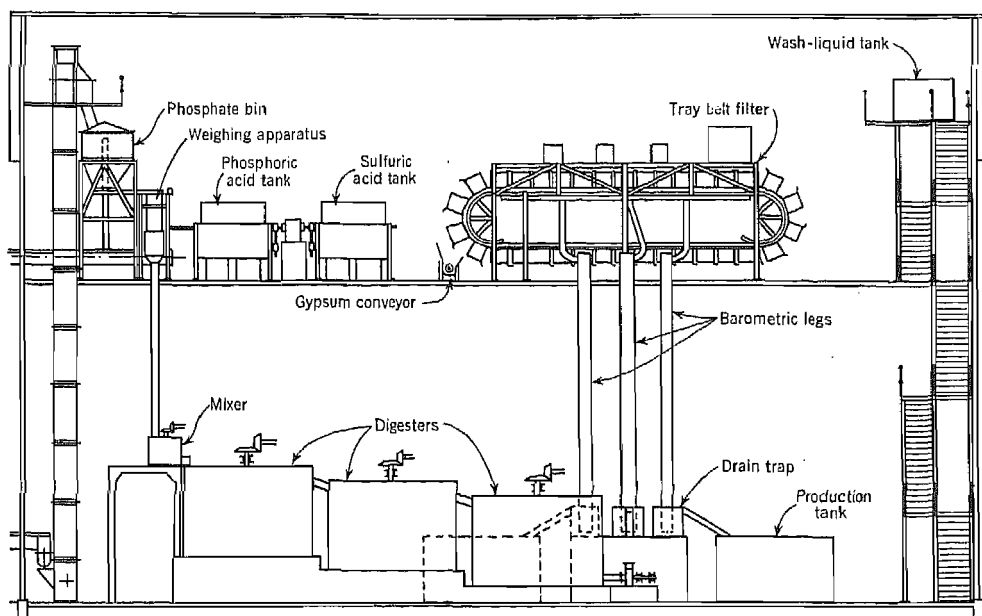


Fig. 10. Manufacture of wet-process phosphoric acid (dihydrate process) (44).

The growth of crystals may be increased by returning sludge from the last agitator to the first, or by adding gypsum crystals,  $CaSO_4 \cdot 2H_2O$ , from the filter to the first agitator. Owing to the comparatively low temperature and concentration of mother liquor, ordinary wool cloth can be used for filtering purposes.

The drawbacks of the process are relatively low yield, long reaction time, and the necessity of concentrating the acid produced in order to reach the 47–50%  $P_2O_5$  concentration needed for production of double superphosphate.

In 1926, there were no suitable filters for filtering a hot phosphoric acid slurry containing up to 33%  $P_2O_5$ . A continuous-working, horizontal filter of a new design was invented by Wallny at Landskrona, Sweden (see Fig. 10). This filter was later manufactured by the Lurgi Company and sold as the Lurgi filter. It is in use in several European countries and the U.S.

While Nordengren and associates developed the strong-acid process in Sweden, the Dorr Company in the U.S. and the Kunstdünger-Patent-Verwertungs-A.-G. of

Phosphoric acid obtained from the filter has to be concentrated to about 35%  $P_2O_5$  for the production of monoammonium phosphate and to about 45-55%  $P_2O_5$  for triple superphosphate. One concentration method is to burn fuel oil or gas in compressed air and to inject the combustion gases under pressure into the acid. In another method, combustion gases or heated air is forced through a packed or empty tower into which the dilute acid is sprinkled. In this process a certain amount of

$P_2O_5$  is volatilized with the steam. In some recent installations Swenson hard-lead vacuum evaporators are used in parallel or in series.

A wet-process phosphoric acid plant designed by the Dorr Company, Inc., New York, patentees of the wet process, is operated by the Consolidated Mining and Smelting Company, Limited, at Trail, B.C. Strong production acid containing 32-33%  $P_2O_5$  is produced in the leaching process. The phosphoric acid section consists of 3 units in parallel, each designed to treat 150 tons of phosphate rock per day. Originally the phosphoric acid was used for production of triple superphosphate. Now, all is used in the manufacture of ammonium phosphate. See Figure 11.

Undried phosphate rock produced in Garrison, Montana, is shipped as mine-run material to Trail. The phosphate rock is broken down by jaw and gyratory crushers followed by rolls. Some of the rock is dried in rotary dryers to 1% moisture and is then ground in mills provided with air classifiers. The remaining undried phosphate rock is ground in rubber-lined pebble mills. Phosphoric acid (sp.gr. 1.20, 20%  $P_2O_5$ ) is fed by Howard acid feeders to weir boxes placed at the head of each pebble mill. The acid is the first filtrate from the pick-up cycle of the second stage filter.

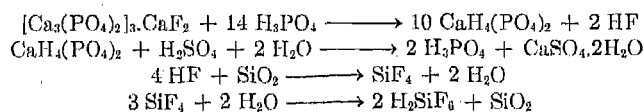
The crushed but unground rock is fed to the pebble mills by Schaffer poidometers. Frequent check weights are taken to make certain that the poidometer feeds within an accuracy of approximately  $\pm 1\%$ . Grinding of the crushed phosphate rock is accomplished partly in dry mills and partly in wet mills. In the wet mills the phosphate rock being ground reacts with phosphoric acid, forming monocalcium phosphate, and with very dilute sulfuric acid, forming gypsum and phosphoric acid.

The first-stage reaction circuit comprises the agitator tanks either constructed of wood, lined with hard sheet lead and Duro brick, or hard lead, brick-lined, with a supporting skeleton of steel bands on the outside of the agitator. The covers are wood decking. The electric motor-driven agitators are interconnected at the top by hard-lead launders and each is equipped with a stainless-steel shaft and propeller. Two air-cooling boxes constructed of heavy, hard-lead plate are submerged under several inches of slurry in each of the agitators 3, 4, and 5. Air is blown into these boxes and through the slurry to control the temperature of the slurry by evaporation cooling. All agitators are vented through ducts to exhaust fans; the gases are treated for recovery of fluorine and finally scrubbed in a water tower before exhausting to the atmosphere.

The slurry discharging from the pebble mills flows by launder into the No. 1 agitator on each unit. Fine dry-ground rock is conveyed by a screw conveyor to a point near the center of the No. 1 agitator on each unit. The fine rock constitutes approximately 35% of the total phosphate rock feed. Sulfuric acid (93%) and first-filtrate phosphoric acid (20%  $P_2O_5$ ) are measured, the former by 4-in. Fischer-Porter rotameters and the latter by the Howard bucket-type feeders. These acids flow into the mixing box. Air is blown into the mixed acid and the fluorine evolved is exhausted to a fluorine-recovery unit. The mixed acid flow leaving the box is split in the proportion desired by means of a weir, and flows by separate hard-lead launders to agitator 3, 4, or 5.

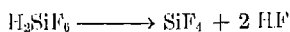
Approximately 800 gal. per minute of slurry is recirculated from each of the Nos. 4 and 5 agitators discharging into the pebble-mill discharge launder where it enters agitator 1. The circulating pulp has a slight excess of sulfuric acid. The  $P_2O_5$  content of the acid present in the circulating pulp is held to approximately 34%. This condition is maintained by proper addition of wash water used in washing the final gypsum, and careful control of extraneous wash water entering the system from such sources as washing down floors, agitators, and other equipment. Solids in the pulp average 45% by weight. The precipitated gypsum is well within the gypsum phase region and the crystals formed are readily filterable. Good agitation greatly assists in preventing highly supersaturated zones of either excess lime or excess sulfuric acid in the reacting slurry at agitator 1, and to a lesser degree in the succeeding agitators in the reaction circuit; thus, the tendency for formation of very small gypsum crystals is reduced. Retention time in the first-stage reaction circuit is 6.5 hours and is ample for the treatment of 650 tons of Montana phosphate rock per 24 hours. More than 99% of the phosphate rock reacts to produce phosphoric acid in this circuit. The reaction is very rapid in the first agitator with a noticeable slowing up in the succeeding agitators.

The main reactions in the first stage are decomposition of phosphate rock by phosphoric acid:





The fluosilicic acid in contact with either phosphoric or sulfuric acid at high temperature decomposes:



The first-stage filters treat a constant flow from agitator 5 of reacted slurry containing 45% solids (largely  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), phosphoric and sulfuric acids, and both dissolved and undissolved fluosilicates. There are two  $12 \times 12$  ft. Dorreo vacuum filters in parallel and a third as a spare. Each filter operates continuously for 16 hours and is then taken out of service for washing and maintenance. Ports for removal of filtrate and air are cut in the bottom and at the center of each filter panel. Production acid (32–33%  $\text{P}_2\text{O}_5$ ) drains out of the ports through 2-in. hard-lead pipes running longitudinally on the outside of the shell around the discharge end of the filter and into the head valve. Drainage of acid from the head valve is through a rubber hose into a filtrate receiver, and then through barometric legs of hard-lead pipe into pump sumps situated approximately 30 ft. below the filter. The filter medium used is a coarse backing cloth of Vinyon over which is placed Vinyon cloth of finer weave. The filter panels are separated by longitudinal lead bars bolted through the sheet-lead lining and steel filter shell.

No washing of the gypsum is done in the first-stage filter and the entire cycle from the bottom of the filter to the top is utilized for separating production phosphoric acid from gypsum. The gypsum cake containing 30–35% by weight of liquor (32–33%  $\text{P}_2\text{O}_5$ ) is blown off at the top of the filter and discharged into a stainless-steel repulp hopper. The vacuum used in the filtration averages 20 in. Hg. Phosphoric acid of concentration of 15.5%  $\text{P}_2\text{O}_5$  (second filtrate) flows continually into the repulp hopper and mixes with the gypsum cake. The source of this acid is the wash cycle of the second-stage filter step. The pulp flows by gravity down a hard-lead launder into the first-stage repulp agitator.

The function of the first-stage repulp agitator is to mix the gypsum cake with second-filtrate phosphoric acid to produce a pulp which can be readily pumped into the agitators of the second-stage reaction circuit. Retention in this agitator is approximately 20 minutes. The agitator is  $12\frac{1}{2}$  ft. in diameter and 11 ft. high, of wood-stave construction lined with sheet lead and Duro acidproof brick. Agitation is provided by a motor-driven stainless-steel agitator shaft and propeller, similar to the equipment used in the first-stage reaction agitators.

The pulp averages 38% solids by weight, and 20.9%  $\text{P}_2\text{O}_5$  and 2.5%  $\text{H}_2\text{SO}_4$ . Slurry is drawn from a point approximately 3 ft. from the top of the agitator into a 4-in. Model C Willey stainless-steel sand pump, equipped with a control valve on the suction line, and is delivered through a 4-in. hard-lead line to the second-stage reaction circuit.

This second-stage reaction circuit consists of four agitators in series, of the same construction as the first-stage repulp agitators in series, with a total retention time in the circuit of 2.1 hours. The temperature is controlled by addition of low-pressure steam direct to the No. 2 agitator. Less than 1% of the reaction of phosphate rock is completed in this circuit. The principal reason for utilizing four agitators is not for reaction of undissolved rock, but to promote formation of larger gypsum crystals and sodium fluosilicate. If this is not accomplished at this point, blinding of the second-stage filter cloth becomes more pronounced and troublesome.

The second-stage filters receive slurry (38% solids by weight and containing phosphoric and sulfuric acids) continuously from the top of the fourth agitator of the second-stage reaction circuit. There are two  $12 \times 12$  ft. Dorreo vacuum filters operating in parallel with a third filter as a stand-by. The liquor from this filtration is termed first filtrate and contains 20%  $\text{P}_2\text{O}_5$ . The cake is washed, and the wash liquor is termed second filtrate and contains 15.5%  $\text{P}_2\text{O}_5$ . The cake on reaching the top of the filter drum is blown off into a stainless-steel repulp hopper within the filter. The first and second filtrates are separately removed by dry vacuum pumps through barometric legs to collecting sumps 25 ft. below the filtrate receivers. The cake is flushed out of the filter repulp hoppers with a continuous stream of fourth filtrate (2.5%  $\text{P}_2\text{O}_5$ ) passing through a perforated pipe. The slurry then flows by gravity to the second-stage repulp agitator.

The function of the second-stage repulp agitator is to mix the gypsum cake with fourth filtrate phosphoric acid to produce a pulp which can be readily pumped to the third-stage reaction circuit. The pulp averages 37% solids by weight and the acid contained in it is 3.5%  $\text{P}_2\text{O}_5$  and 2.5%  $\text{H}_2\text{SO}_4$ . The pulp is drawn from a point approximately 3 ft. from the top of the agitator and delivered to the third-stage reaction circuit, which consists of two agitators in series, and where the total retention time is one hour. The temperature of the circuit averages 60°C. and no extraneous heat is used to maintain the temperature. If necessary, sufficient new sulfuric acid is added to give a content of 2.5% to

further the reaction of the undissolved portion of phosphate rock and also to insure solution of any iron or aluminum phosphate which might otherwise precipitate out on the third-stage filter cloth and cause blinding of the cloth.

The slurry leaving the second of the third-stage agitators flows by gravity to the third-stage filters, which are three Dorco vacuum filters in parallel, with two additional filters as stand-by equipment. The third filtrate contains 3.5%  $P_2O_5$ . The cake moving up on the inside of the drum is subjected to a warm-water wash at 65°C. The wash cycle extending over five panels removes the fourth filtrate (2.5%  $P_2O_5$ ). The cake, when it reaches the vertical position of the filter, is blown off into a stainless-steel repulp hopper within the filter. Water is used to sluice the washed gypsum cake out of the filter and by a wood launder to a 4-in. bronze Wilfley sand pump to waste.

Phosphoric acid flows from the filter barometric legs into hard-lead seal boxes and is pumped to wood-stave, lead-lined storage tanks. All acid lines are of hard lead (7-10% antimony) flanged every 10 ft.

Table XIX gives typical analyses of phosphate rock and production phosphoric acid.

TABLE XIX. Typical Analyses of Phosphate Rock and Production Phosphoric Acid.

	Constituent, %						
	$P_2O_5$	CaO	$Al_2O_3 + Fe_2O_3$	F	$H_2SO_4$	$SiO_2$	$H_2O$
Phosphate rock.....	31.7	44.0	2.8	3.4	—	15.7	1.0
Production phosphoric acid...	33.0	—	2.0	2.0	3.3	—	—

Source: reference (2).

### Triple Superphosphate

Triple superphosphate usually contains from 43 to 50% available  $P_2O_5$ . Most of the phosphoric acid used in the U.S. for triple superphosphate manufacture is derived from the wet process. Some, however, is obtained by the TVA by the electric-furnace process.

In 1872, triple superphosphate was for the first time produced commercially in Germany from low-grade phosphate. Production of triple superphosphate in the U.S. began about 1900. Before 1907, the total production was probably not in excess of 2000 tons. Table XX (36) gives the production for some years beginning with 1907.

TABLE XX. U.S. Production of Triple Superphosphate.

Year	Production, tons <sup>a</sup>	Year	Production, tons <sup>a</sup>
1907.....	1,800	1940.....	329,046
1910.....	6,177	1945.....	262,737
1920.....	15,256	1948.....	468,711
1930.....	95,198	1949.....	549,000

<sup>a</sup> 45% basis.

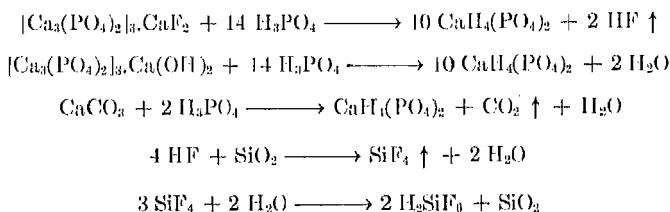
Up to 1914, all triple superphosphate produced in the U. S. was made with phosphoric acid produced by the wet process. In 1914, the Piedmont Electro Chemical Company in Mount Holly, N.C., made phosphoric acid by the electric-furnace process for the express purpose of making triple superphosphate. The furnace was a large unit with three 20-in. carbon electrodes. The cheap electric power expected did not

materialize and after producing 10,000–12,000 tons of triple superphosphate and about 2,000–3,000 tons of ammonium phosphate, the plant was abandoned.

In 1931, the Victor Chemical Works at Nashville, Tennessee, produced blast-furnace phosphoric acid for triple superphosphate. No phosphoric acid has been made by the blast-furnace process for triple superphosphate manufacture in recent years.

In 1922, the Anaconda Copper Company started producing triple superphosphate by the wet process. A year or two later the first plant was superseded by a larger one. In 1931, the Consolidated Mining & Smelting Company of Trail, B.C., Canada, began manufacturing triple superphosphate. The plant was equipped to produce the triple superphosphate or ammonium phosphate, whichever was in greatest demand. After 1931, several new wet-process phosphoric acid plants and the TVA electric-furnace process plant for making triple superphosphate were constructed.

The principal reactions which occur in the manufacture of triple superphosphate are probably:



If hot and concentrated phosphoric acid is used for acidulating phosphate rock, a fair amount of fluorine-containing gases is liberated; however, the amount is less than in the production of ordinary superphosphate. With dilute and cold phosphoric acid, practically no fluorine compounds are volatilized.

If the amount of impurities in phosphate rock used for acidulation is low, the ratio of  $\text{P}_2\text{O}_5$  from phosphoric acid to  $\text{P}_2\text{O}_5$  from phosphate rock would be about 2 for 95% conversion. If, however, the quantity of impurities is relatively larger, then a number of side reactions take place which require a ratio larger than 2.

In the acidulation of Florida land-pebble phosphate rock, the desired ratio of  $\text{P}_2\text{O}_5$  from phosphoric acid to  $\text{P}_2\text{O}_5$  from phosphate rock is 2 or slightly above it. On the other hand, with Tennessee rock a ratio of 2.4–2.6 may be desirable.

If 70–78%  $\text{H}_3\text{PO}_4$  (51–56.5%  $\text{P}_2\text{O}_5$ ) is available for acidulation of phosphate rock, the resultant product will be sufficiently dry after adequate cure to make artificial drying unnecessary. Phosphoric acid of any desired strength can be obtained readily from acid produced by the blast or electric furnace. Wet-process phosphoric acid containing up to 56%  $\text{P}_2\text{O}_5$  can be obtained with vacuum-type evaporators.

70–78%  $\text{H}_3\text{PO}_4$  at 110°F. and higher reacts sufficiently rapidly with phosphate rock to cause the slurry to set within 3 or 4 minutes after mixing. This property makes possible a fairly simple continuous process for making triple superphosphate. Figure 12 shows a flow sheet of a continuous process used by the TVA for making triple superphosphate from phosphate rock and phosphoric acid with a 70–78%  $\text{H}_3\text{PO}_4$  content. The phosphate rock and acid are mixed for a few seconds in a funnel-type mixer in which all agitation is provided by the acid which is introduced tangentially into the mixer. The detailed description of the equipment used and the investigational work conducted can be found in a publication of the TVA (5).

If high-strength wet-process phosphoric acid of 70–78%  $\text{H}_3\text{PO}_4$  is not available,

relatively weak phosphoric acid can be used for acidulating phosphate rock. The resultant product will contain a high percentage of moisture and requires drying before it is ready for use. Since the undried product is rather sticky, it is customary to add dried material to the undried product in order to decrease the tendency to form large lumps and caking on the walls of the dryer. A manufacturer may also decide not to concentrate the phosphoric acid as far as 70%  $\text{H}_3\text{PO}_4$  and to carry out drying of the resultant triple superphosphate in preference to evaporation of the original acid.

The freshly made superphosphate is normally allowed to cure for one to three months before shipping. During the curing process the free  $\text{H}_3\text{PO}_4$  content is reduced and some undigested phosphate rock is converted to available  $\text{P}_2\text{O}_5$ .

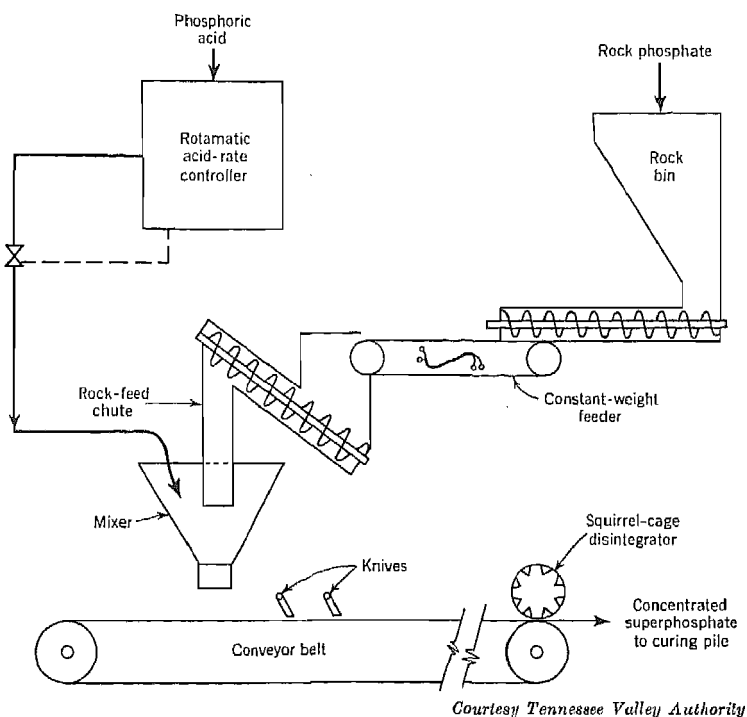
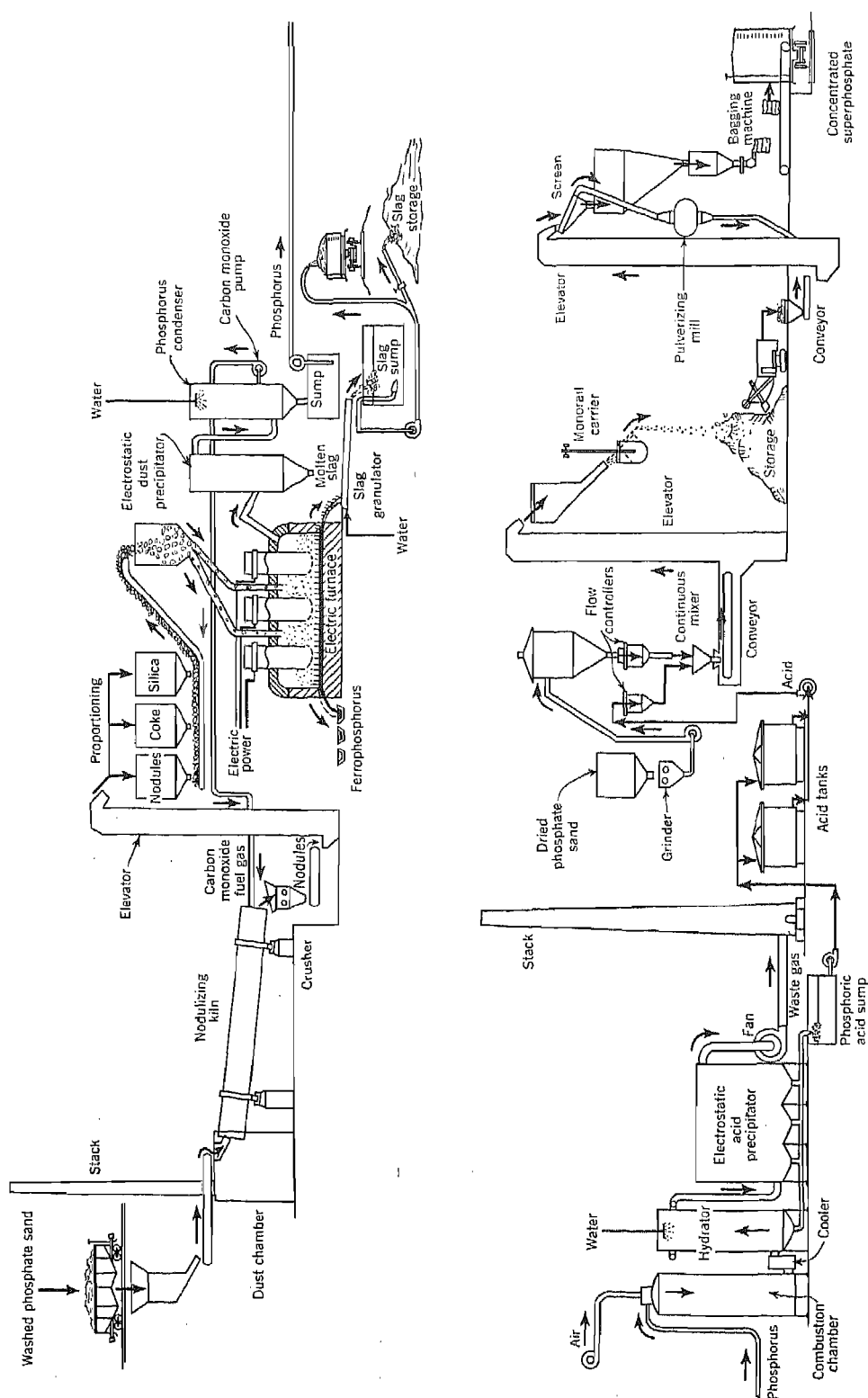


Fig. 12. Continuous process for the manufacture of triple superphosphate.

If it is desired not to cure the triple superphosphate for several months and yet have it in good condition for quick shipment, the fresh superphosphate can be dried advantageously in Roto-Louvre dryers.

**Electric-Furnace Method.** The TVA is the only manufacturer using this method, since quantities of cheap electric power are necessary. The Authority terms the product "concentrated" superphosphate, as opposed to the more common "triple superphosphate."

In this process (see Fig. 13) a proportioned charge of lump or agglomerated phosphate rock, coke, and silica is smelted in an electric furnace to produce elemental phosphorus. By-products of the furnace process include carbon monoxide gas, calcium silicate slag, ferrophosphorus, and furnace dust. Elemental phosphorus leaves the furnace as a vapor in admixture with carbon monoxide. The gas mixture first passes



*Courtesy Tennessee Valley Authority*

Fig. 13. Electric-furnace method for the manufacture of concentrated superphosphate (5).

through an electrostatic precipitator to remove entrained dust, and then enters a condenser into which water is sprayed. Upon cooling of the gas mixture by the water, the phosphorus condenses to liquid form, leaving the carbon monoxide available for use as a fuel.

Molten slag and ferrophosphorus are tapped from the furnace periodically. The molten slag is quenched and granulated by the action of high-velocity jets of water; the resultant material finds use as an agricultural liming material. The ferrophosphorus is tapped into molds, and after cooling is separated into various grades according to phosphorus content. A portion of the ferrophosphorus produced is used by the steel industry. The furnace dust removed from the electrostatic precipitator contains both potash and phosphate, but is not produced in sufficient quantities to be used as a fertilizer.

Phosphoric acid is produced from elemental phosphorus by oxidizing the phosphorus with air and absorbing the resulting phosphorus pentoxide vapor in water. The oxidation of phosphorus is carried out in a water-cooled tower constructed of graphite blocks. The phosphorus pentoxide is treated with water in an acidproof brick tower, and liquid phosphoric acid is withdrawn from this tower. A portion of the acid passes through the tower in the form of a mist which is collected in an electrostatic precipitator constructed mainly of carbon and acidproof brick. The phosphoric acid contains about 83%  $\text{H}_3\text{PO}_4$ .

In making concentrated superphosphate, the phosphoric acid is diluted to 78%  $\text{H}_3\text{PO}_4$ , and is mixed with pulverized phosphate rock in a continuous mixer. The acid-rock mixture leaves the mixer in the form of a slurry which sets to solid form in about 12 seconds. The fresh superphosphate is cured in storage piles for about 90 days. Thereafter the cured superphosphate is dug out of the piles and is crushed, screened, and bagged for shipment.

The TVA gives process requirements for the manufacture of phosphoric acid and concentrated superphosphate by the electric-furnace method as shown in Table XXI.

**TABLE XXI. Manufacturing Data for Phosphoric Acid and Superphosphate by the Electric-Furnace Method.**

Material or service	Requirements	
	Per ton $\text{P}_2\text{O}_5$ in acid	Per ton avail. $\text{P}_2\text{O}_5$ in superphosphate
Phosphate for furnaces, tons.....	4.15	2.98
Phosphate for acidulation, tons.....	—	1.03
Coke (87% fixed carbon), tons.....	0.78	0.56
Silica (96% $\text{SiO}_2$ ), tons.....	0.51	0.36
Power, kw.-hr.....	5,760	4,165
Water, raw, gal.....	20,720	14,870
Water, filtered, gal.....	720	530
Electrodes, lb.....	20	15

The requirements for the raw materials, phosphate, coke, and silica, will vary from those given in Table XXI, depending on the analysis of the phosphate rock employed. The figures given apply to a dry, agglomerated phosphate for furnace burden, which contains 28.3%  $\text{P}_2\text{O}_5$ , 39.9%  $\text{CaO}$ , 20.4%  $\text{SiO}_2$ , and 2.6%  $\text{Fe}_2\text{O}_3$ . The phosphate for acidulation contains 32.4%  $\text{P}_2\text{O}_5$ .

In proportioning the charge for the electric furnace, the percentages of phosphoric acid, lime, silica, and iron oxide in the phosphate rock are determined by analysis. The coke added to the charge is the amount necessary to reduce all the phosphoric acid in the furnace charge to elemental phosphorus and all the iron oxide to iron, plus 2–4%. Silica is added in an amount sufficient to give a ratio, by weight, of  $\text{SiO}_2$  to  $\text{CaO}$  in the charge equal to about 0.8.

### Defluorinated Phosphate Rock

In 1934, the U.S. Department of Agriculture reported that in laboratory experiments in excess of 95% of the fluorine had been removed from phosphate rock. A small charge of finely ground phosphate rock in thin layers was heated in an electric furnace at  $1400^\circ\text{C}$ . in the presence of steam. Better than 80% of the  $\text{P}_2\text{O}_5$  content was rendered soluble in neutral ammonium citrate. The product was caked or sintered but not fused. The principal reaction was probably:



Fluorapatite is very insoluble, but  $[\text{Ca}_3(\text{PO}_4)_2]_3 \cdot \text{Ca}(\text{OH})_2$  is soluble in ammonium citrate solution, if finely ground. Thus, the removal of the fluorine makes the phosphorus available as a fertilizer; if the product is to be used as an animal feed, the fluorine must be removed owing to its toxic nature.

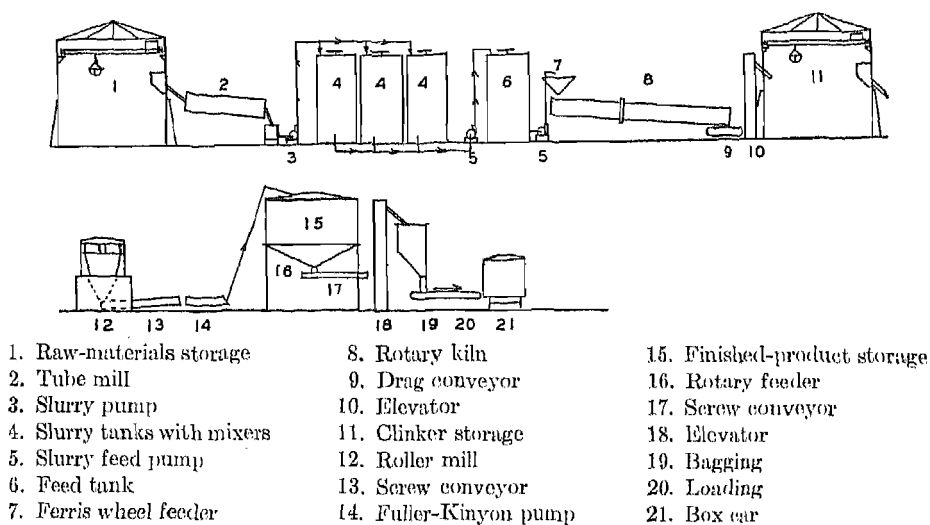


Fig. 14. Defluorination plant (66).

The Coronet Phosphate Company at Plant City, Florida, produces defluorinated phosphate rock by calcining without fusion in rotary kilns (66). From June 1944 to June 1946 approximately 115,000 short tons of product was made. Approximately 25,000 tons was used for direct application to the soil. The major portion was supplied to the feedstuff industry. Since about the middle of 1946, most of the defluorinated phosphate produced by the Coronet Phosphate Company has been used by the feedstuff industry.

Florida pebble phosphate rock containing 34–35%  $\text{P}_2\text{O}_5$  and tailings from the

flotation plant containing 90%  $\text{SiO}_2$  are ground separately in a  $7 \times 35$  ft. Traylor tube mill (see Fig. 14). Water is added to the feed to form a slurry containing 35–45% water. The raw materials are ground to about 85% through a 200-mesh screen. The slurry from the mill is pumped to one of the slurry tanks with mixers. The two materials are then blended so that the feed to the kiln contains 42–45%  $\text{SiO}_2$  and 55–58% phosphate rock on a dry basis. Two kilns  $6\frac{1}{2}$  ft. in diameter and 135 ft. long (oil-fired) are used with temperatures in the burning zone of 2700–2900°F. The load remains in the 30 ft. burning zone 20–30 minutes. Water vapor is introduced at the hot end of the kiln. The load is quenched as it is discharged from the kiln by jets of water. This produces the excess of water vapor necessary for effective defluorination. The rapid cooling of the clinker prevents the  $\alpha$ -tricalcium phosphate formed at defluorinating temperatures from reverting to the beta form with its lower availability. The kiln product consists of grayish green nodules closely resembling cement clinker. The product is ground and is free-flowing, nonhygroscopic, and insoluble in water. Typical analyses of the Coronet product are given in Table XXII.

TABLE XXII. Analyses of Three Samples of Coronet Defluorinated Phosphate Rock.

Constituent	Amount, %		
$\text{P}_2\text{O}_5$ total	20.55	21.01	20.59
$\text{P}_2\text{O}_5$ available in 0.4% HCl	19.86	20.56	20.34
$\text{P}_2\text{O}_5$ available in 2% citric acid	19.56	19.83	19.14
$\text{P}_2\text{O}_5$ available in neutral ammonium citrate	18.58	18.01	18.59
CaO	28.80	28.77	28.58
$\text{Fe}_2\text{O}_3$	0.87	0.83	1.03
$\text{Al}_2\text{O}_3$	0.76	0.71	0.65
Fluorine	0.02	0.06	0.08
Insoluble siliceous matter	48.65	47.64	48.20

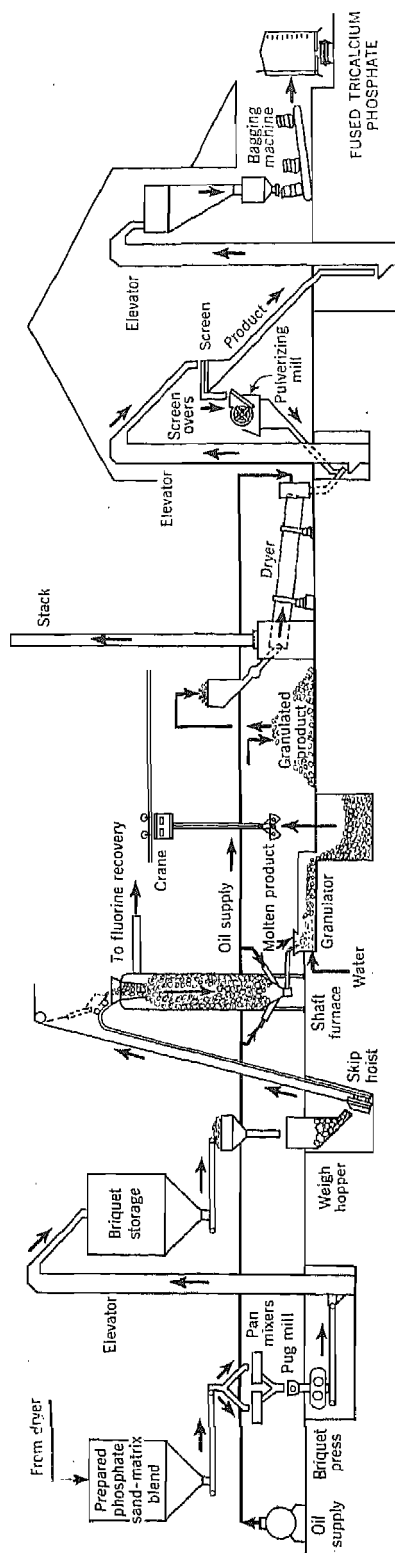
### Fused Tricalcium Phosphate

Fused tricalcium phosphate, a fertilizer material containing about 28% citrate-soluble  $\text{P}_2\text{O}_5$  and not more than 0.4% fluorine, is produced by fusing raw lump phosphate rock or agglomerated phosphate sand in an oil-fired shaft furnace (see Fig. 15). Defluorination of the phosphate rock or sand is accomplished by the action of water vapor produced in combustion of the oil. The molten phosphate is quenched and granulated by high-velocity water jets as it is tapped from the furnace, and is prepared for shipment as a –10 mesh product by drying, screening, and grinding the small percentages of +10 mesh oversize. Fluorine evolved from the phosphate rock is recovered in a limestone-packed tower. Since the product is not water-soluble or hygroscopic, it may be stored outdoors and shipped in open cars and in inexpensive paper bags.

TABLE XXIII. Manufacturing Data for Fused Tricalcium Phosphate.

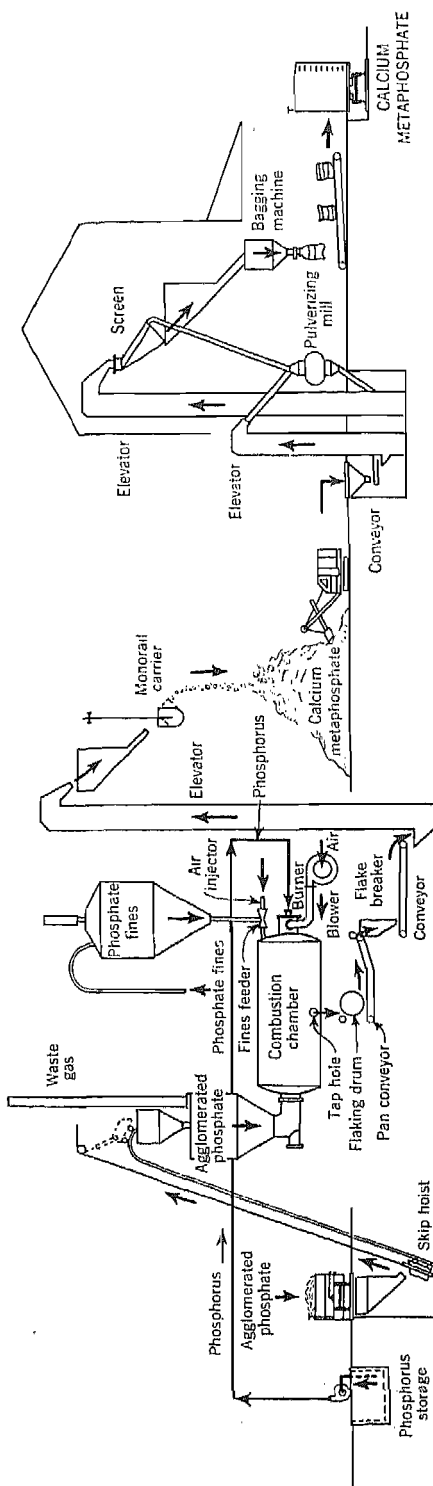
Material	Requirements per ton of product
Phosphate rock, dry basis, tons.....	1.12
Fuel oil, furnace only, gal.....	50
Fuel oil, product drying, gal.....	5
Air, furnace only, cu.ft. (S.T.P.).....	70,000
Water, gal.....	4,000





*Courtesy Tennessee Valley Authority*

Fig. 15. Manufacture of fused tricalcium phosphate.



*Courtesy Tennessee Valley Authority*

Fig. 16. Manufacture of calcium metaphosphate.

Pilot-plant experiments have shown that gaseous fuels can be used in the furnace, and tests on the use of pulverized coal as a fuel are being carried out.

The process requirements given in Table XXIII are based on operation of TVA's demonstration plant at Columbia, Tennessee.

### Calcium Metaphosphate

Calcium metaphosphate, the product of the reaction between phosphate rock and hot phosphorus pentoxide, contains more than 60% available  $P_2O_5$ . Figure 16 is a flow sheet illustrating its manufacture.

In a furnace, liquid phosphorus is burned in a horizontally mounted, cylindrical combustion chamber to form phosphorus pentoxide that reacts with pulverized phosphate rock blown into the chamber at a point just above the phosphorus burner. Molten calcium metaphosphate formed by this reaction collects in a pool on the floor of the combustion chamber. Hot gases containing unreacted phosphorus pentoxide leave the combustion chamber and enter a tower filled with lump or agglomerated phosphate. In this tower the remaining phosphorus pentoxide reacts with the lump phosphate to form additional calcium metaphosphate which drains from the tower into the metaphosphate pool in the combustion chamber. From 70 to 90% of the phosphate consumed is in the form of pulverized material, and the remainder is in the form of lumps. The molten calcium metaphosphate is tapped continuously from the chamber onto a rotating, water-cooled drum flaker. The cooled metaphosphate flakes are conveyed to a storage bin and from there to crushers, screens, and bagging machines. Although calcium metaphosphate does not require any curing, facilities are provided for seasonal storage of the flaked material.

The process requirements for producing one ton of  $P_2O_5$  in the form of calcium metaphosphate are about equal to the requirements for producing one ton of  $P_2O_5$  in triple superphosphate made by the electric-furnace method.

### Calcium Magnesium Phosphate

A fused phosphate which is finely ground containing 19% available  $P_2O_5$  by the A.O.A.C. neutral ammonium citrate method is produced by Manganese Products, Incorporated, Seattle, Washington (43). It is made in a modified three-phase Greene electric-arc steel-melting furnace from two parts phosphate rock and one part olivine. The process was originally developed by the TVA. Montana phosphate rock crushed to -1.5 in., containing 30-32%  $P_2O_5$ , and olivine,  $(Mg,Fe)_2SiO_4$ , crushed to -1.5 in., containing 8%  $Fe_2O_3$ , are used as feed. Each charge contains from 5 to 6.5 tons. The furnace operates at 5000 amp. and 180 v. The power consumption is 850 kw.-hr. per ton of product. The temperature in the melting zone at the bottom of the furnace ranges from 1500 to 1600°C. The fusion time is 1-2 hours.

Practically all  $P_2O_5$  in the charge appears in the final product. Much of the iron in the olivine is reduced to the metallic state, and is tapped at the lower hole in the furnace. 80-90% of the fluorine remains in the product.

The molten phosphate slag is quickly quenched with spray water. Slow cooling will cause the phosphate to revert to the insoluble form. A typical analysis of the fused phosphate fertilizer is given in Table XXIV. The product is alkaline in reaction and its neutralizing power is equivalent to 1200 lb. limestone per ton of product. Since the final product is alkaline it will not absorb ammonia and is not suitable for

mixing with ammonium salts. Most of the product is used for direct application to the soil without further treatment or addition of other plant nutrients.

TABLE XXIV. Analysis of Fused Phosphate Fertilizer.

Constituent	Per cent	Constituent	Per cent
P <sub>2</sub> O <sub>5</sub> total.....	22.5	MnO.....	0.25
P <sub>2</sub> O <sub>5</sub> available <sup>a</sup> .....	19.0	B <sub>2</sub> O <sub>3</sub> .....	0.04
CaO.....	29.0	V <sub>2</sub> O <sub>5</sub> .....	0.15
MgO.....	14.0	CuO.....	0.01
SiO <sub>2</sub> .....	23.0	TiO <sub>2</sub> .....	0.15
F.....	1.8	ZnO.....	0.03
R <sub>2</sub> O <sub>3</sub> .....	7-8	NiO.....	0.08
Ni <sub>2</sub> O.....	0.30	SrO.....	0.30
K <sub>2</sub> O.....	0.50	Cr <sub>2</sub> O <sub>3</sub> .....	0.30
BaO.....	0.10		

<sup>a</sup> Neutral ammonium citrate method for P<sub>2</sub>O<sub>5</sub>.  
Source: reference (43).

### Raw Materials and Power Requirements

Table XXV compares the raw material, fuel, and power requirements for making various phosphate fertilizer products.

In the manufacture of phosphate fertilizer, cost of equipment, buildings, labor, freight rates, and suitability of product as a plant nutrient are important factors in choosing a product and process. The cost of raw materials, fuel, and power required are other factors deserving attention in the geographical location of a manufacturing plant.

The electric-furnace process for producing triple superphosphate and calcium metaphosphate requires cheap coke and cheap electric power to be competitive. The blast-furnace process for making triple superphosphate needs low-cost coke, and fused phosphate requires cheap fuel oil or natural gas. The process for making fused calcium magnesium phosphate requires low electric-power rates. Since low-cost coke, fuel oil, and electric power are not available in many of the heavy fertilizer-consuming areas,

TABLE XXV. Raw Materials, Fuel, and Power Requirements to Produce 1 Ton of P<sub>2</sub>O<sub>5</sub> Equivalent.

	Triple superphosphate			Calcium meta-phosphate, 0-63-0	Fused phosphate, 0-30-0	Fused calcium magnesium phosphate, 0-20-0	Defluorinated phosphate rock, 0-20-0	Ordinary super-phosphate, 0-20-0
	Wet process, 0-45-0	Electric furnace, 0-45-0	Blast furnace, 0-45-0					
Phosphate rock, tons	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Sulfur, tons	0.6	—	—	—	—	—	—	0.6
Silica, tons	—	0.8	0.8	0.8	0.4	—	2.85	—
Coke, tons	—	0.5	1.8	0.5	—	—	—	—
Power, kw.-hr.	—	4,100	—	4,100	—	4,000	—	—
Fuel oil, gal. <sup>a</sup>	—	—	—	—	240	—	240 <sup>b</sup>	—
Natural gas, cu.ft. <sup>a</sup>	—	—	—	—	33,000	—	—	—
Magnesium silicate, tons	—	—	—	—	—	1.8	—	—

<sup>a</sup> Use either fuel oil or natural gas.

<sup>b</sup> Estimated.

most of the high-analysis fertilizer phosphates are produced by the less expensive wet process. Calcium metaphosphate, fused phosphate, and fused calcium magnesium phosphate also have the drawback that they do not combine with anhydrous ammonia and ammoniating solutions. On many soils the fused phosphate and fused calcium magnesium phosphate are much less available to plants as nutrients.

### POTASH-CONTAINING MATERIALS

Before World War I, the U.S. depended upon imports of German and French potash salts. Immense natural deposits of potassium chloride occur in several parts of Europe, but when imports were cut off during World War I, a number of make-shift sources were developed in the U.S. including extraction from seaweed, low-grade salts from dry lakes in Nebraska, and waste material from sugar-beet factories. The one source located during World War I which is still of importance is Searles Lake, a dry lake at Trona, California. Another dry-lake source is Salduro Marsh, Utah. The domestic mineral deposits of potassium chloride of present-known commercial work-

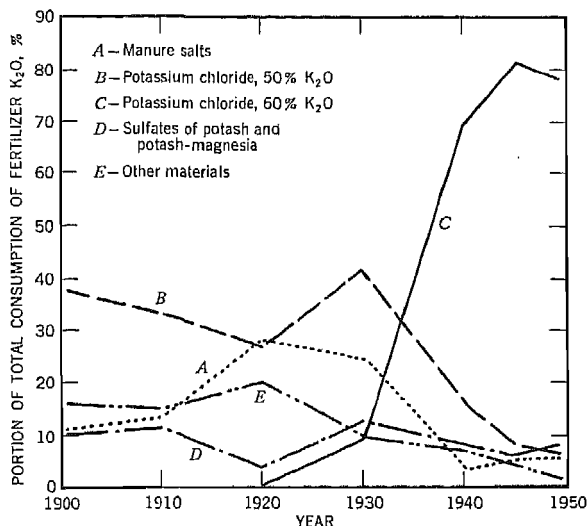


Fig. 17. Relative consumption of various potash-containing materials from 1900 to 1949.

ability are limited to four isolated sylvite deposits near Carlsbad, New Mexico. Reserves of potassium sulfate of proved economic importance are limited to a langbeinite bed in the Carlsbad region, New Mexico. Compared with these deposits, potash reserves in the workable brines of California and Utah are of much smaller magnitude. See also *Potassium compounds*.

Consumption of agricultural potash in the U.S. according to the National Fertilizer Association is shown in Table XXVI, and the percentage of potash derived from various materials is shown in Figure 17.

**"Double Sulfate of Potash Magnesia,"**  $K_2SO_4 \cdot 2MgSO_4$  (the term "double" refers to the  $2MgSO_4$  in the formula and is in contrast to "single sulfate of potash magnesia,"  $K_2SO_4 \cdot MgSO_4$ ). The only domestic source is the langbeinite deposits of New Mexico, which are refined and marketed under the trade name Sul-Po-Mag by the International

Minerals and Chemical Corporation. It is used in quantity as a primary source of water-soluble magnesium and as a supplemental source of potassium sulfate, since it contains 18.5% MgO and 22.6% K<sub>2</sub>O.

TABLE XXVI. Consumption of Agricultural Potash in the U.S.

Year	Consumption, tons K <sub>2</sub> O		Year	Consumption, tons K <sub>2</sub> O	
	Domestic	Imported		Domestic	Imported
1880.....	—	20,000	1945.....	704,000	—
1900.....	—	60,000	1947.....	950,000	45,000
1920.....	40,000	170,000	1948.....	1,032,000	40,000
1930.....	45,000	305,000	1949.....	1,049,000	40,000
1940.....	340,000	70,000			

**"Manure salts"** is the name given to the mineral sylvinite, which is a mixture of sylvite, KCl, and halite, NaCl. This source of potash contains between 20 and 30% K<sub>2</sub>O. It is mined and sold without refining. French and German sources of potash formerly provided the manure salts consumed in the U.S., but the establishment of potash mines in New Mexico has made the U.S. independent of foreign sources.

Because of the high sodium chloride content and relatively low potash content, manure salts are of secondary importance in mixed fertilizers. The hygroscopic character of this material may cause caking or moisture accumulation in mixed goods if used in too great quantities.

Manure salts are used only because the capacities of the potash refineries are not great enough to supply all the potash required in the form of the high-grade chlorides.

**Potassium chloride** (muriate of potash), KCl, occurs in U.S., German, and French deposits only to a small extent in its mineral form, sylvite. The product that is sold on the market as high-grade muriate of potash is a refined product (60-62% K<sub>2</sub>O) secured by removing sodium chloride from sylvinite or by refining brines from the dry lakes of California and Utah. It is the most important source of potash, comprising about 78% of the total consumption in 1949.

**Potassium chloride** (50% muriate of potash) is similar to the high-grade (60-62% K<sub>2</sub>O) potassium chloride except that it has not been so highly refined and contains a certain amount of sodium chloride. With a content of 48-50% K<sub>2</sub>O, its chief use is in direct application, although the domestic potash strike in 1949-50 caused some imported 50% muriate to be used in mixtures.

**Potassium sulfate**, K<sub>2</sub>SO<sub>4</sub>, (the unrefined product (48-50% K<sub>2</sub>O)), is obtained through import and from domestic sources. It is considerably more expensive than the potassium chloride and therefore is used in mixtures only where a minimum chlorine guarantee is necessary, as in fertilizer for tobacco.

Minor sources include "single sulfate of potash magnesia," K<sub>2</sub>SO<sub>4</sub>·MgSO<sub>4</sub>, which contains an average of 9-11% MgO and approximately 25% K<sub>2</sub>O. This was imported from Europe for several years, but none has been imported into the U.S. since World War II.

Another minor source is kainite, MgSO<sub>4</sub>·KCl·3H<sub>2</sub>O. Over the years, the term kainite has covered a wide range of low-potash-content salts imported from Germany. As the high-grade potassium chloride from domestic sources became more important, the lower grades of potash salts declined and what little kainite is used today is a low-grade manure salt containing 15-20% K<sub>2</sub>O, the balance being NaCl.

## PLANT-FOOD RAW MATERIALS CONTAINING OTHER ELEMENTS

**Calcium.** Fertilizers do not supply calcium as a primary ingredient, though it is a constituent of several raw materials. In the North and East, the inexpensive limestone regularly applied to neutralize acid soils supplies adequate calcium to crops. In the South, where lime is costly and more acid-tolerant crops are grown, the calcium in plant foods is an important source of this element.

The principal source of calcium in mixed fertilizers is ordinary superphosphate.

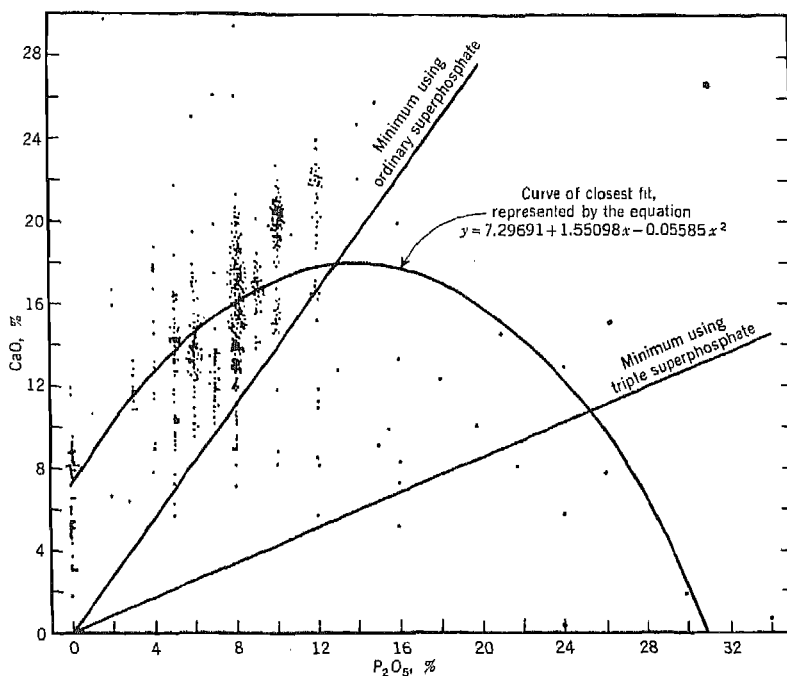


Fig. 18. CaO and  $P_2O_5$  contents of commercial mixed fertilizers (38).

It has supplied more than 70% of the total in every year since 1900 and over 85% in a few years. The next most important source, dolomite, supplied 10% in 1945.

Table XXVII gives the average lime content of the more commonly used plant-food raw materials. Figure 18 shows the lime and phosphoric acid contents of commercial mixed fertilizers. The data represent the CaO content found by chemical analysis in mixtures of the guaranteed phosphoric acid content indicated. The straight lines show the amount of CaO that would be supplied by ordinary and triple super-

TABLE XXVII. Average Lime Content of Some Commonly Used Plant-Food Raw Materials.

Raw material	CaO content, %	Raw material	CaO content, %
Calcium nitrate.....	27.4	Hydrated lime.....	62.52
Cal-Nitro.....	11.40	Limestone.....	44.35
Cyanamid.....	53.89	Phosphate rock.....	46.29
Dolomite.....	30.50	Superphosphate, ordinary.....	27.36
Gypsum.....	31.17	Superphosphate, triple.....	19.99

Source: reference (38).

phosphate at various phosphoric acid levels. The dots falling below the triple superphosphate line represent fertilizers deriving at least a part of their phosphoric acid content from ammonium phosphate. A considerable part of the scatter about the curve is due to varying amounts of dolomite added to render the fertilizer non-acid-forming.

**Magnesium**-containing raw materials include both primary magnesium sources as well as others in which it is only incidentally present. The dolomite employed to render mixed goods non-acid-forming is an important source, since it contains 19.5% MgO. Other important sources include sulfate of potash magnesia, Epsom salts, and calcined dolomite (Kemidol oxide). Many materials not thought of as sources of magnesium but which are used for their content of the principal plant nutrients nevertheless do supply significant amounts.

Dolomite is the largest single source of magnesium, and though it is relatively insoluble in water, its magnesium is available to plants in most acid soils. It also reacts in mixtures with superphosphate to form water-soluble compounds. The average magnesia content of important fertilizer raw materials is given in Table XXVIII.

Like calcium, quantities of **sulfur** are added to the soil in raw materials which are primarily sources of other plant nutrients. Where sulfur is extremely deficient, it is supplied by direct application of gypsum or elemental sulfur. The percentage of  $\text{SO}_3$  in mixed fertilizers as a general rule increases with both the nitrogen and phosphoric acid contents to a total nitrogen, phosphoric acid, and potash content of about 25%. It decreases after that to zero at about 65% total phosphoric acid and potash. Ordinary superphosphate supplies by far the greatest total amount of sulfur, due both to the tremendous tonnages consumed and to its fairly high  $\text{SO}_3$  content.

TABLE XXVIII. Average Magnesia Content of Fertilizer Raw Materials.

Raw material	MgO, %	Raw material	MgO, %
Calcium nitrate.....	2.49	Dolomite.....	19.50
Cal-Nitro.....	7.40	Dolomite, selectively calcined..	27.00
Basic slag, open-hearth.....	5.63	Epsom salt.....	16.00
Superphosphate, triple.....	0.38	Hydrated dolomitic lime.....	29.00
Superphosphate, ordinary.....	0.47	Kieserite, calcined.....	30.50
Potassium chloride, 60%.....	0.09	Magnesia.....	92.00
Potassium sulfate.....	1.10	Magnesite.....	45.00
Potassium magnesium sulfate, domestic..	18.5		

Source: reference (39).

Table XXIX gives the mean  $\text{SO}_3$  content of various fertilizer raw materials. Cyanamid, dolomite, and potassium chloride contain less than 1%  $\text{SO}_3$ , while ammonium nitrate, ammoniating solutions, and sodium nitrate contain little or none.

TABLE XXIX. Average  $\text{SO}_3$  Content of Fertilizer Raw Materials.

Material	$\text{SO}_3$ , %
Ammonium sulfate.....	59.67
Ammonium phosphate sulfate (16-20-0).....	38.49
Triple superphosphate.....	3.40
Ordinary superphosphate.....	29.09
Potassium sulfate.....	44.09
Potassium magnesium sulfate.....	56.76

Traces of **minor elements** are found in any plant-food mixture derived from the usual commercial raw materials. Superphosphate, manure salts, and natural organic nitrogen sources each have small quantities of minor elements included as impurities. When it is desired to supply a definite amount of minor elements, whether guaranteed or not, they are added to the formula in the form of the sulfates of copper, manganese, and zinc, with boron added in the form of sodium tetraborate decahydrate (borax),  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .

The consumption of the sulfates of manganese, copper, and zinc applied to the soil as such or as ingredients of mixed plant foods is given in Table XXX. The figures are approximations in some cases.

TABLE XXX. Probable Consumption of Manganese, Copper, and Zinc Sulfates for Fertilizer Purposes.

Year	$\text{MnSO}_4$ , tons	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , tons	$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ , tons
1930.....	—	305	Trace
1935.....	1,135	1,250	354
1938.....	2,080	2,300	1,250
1940.....	4,700	9,100	—
1942.....	6,800	14,300	4,123
1944.....	26,400	19,747	4,974
1946.....	48,300	32,141	10,816
1947.....	34,000	24,700	13,725
1948.....	40,200	27,300	14,610

Courtesy: J. K. Plummer, Tennessee Corporation.

Since two producers provide all of the borax consumed, tonnage figures are not available. It is probable that borax consumption far exceeds the sum total of the other 3 minor elements.

Molybdenum, required in extremely small quantities by plants, is rarely found to be deficient in soils. Superphosphate contains this element as an impurity, and generally supplies sufficient quantities of the element. Where molybdenum is extremely deficient, very small applications of sodium or ammonium molybdate are made.

## MIXED GOODS

Mixed fertilizers (or mixed goods) are combinations of various plant-food raw materials providing two or more nutrient elements. They are mixed in specially designed equipment to obtain a predetermined formula.

In 1948-49, mixed fertilizers comprised 12,839,506 tons out of the 18,541,885 tons of all fertilizer materials used in the U.S. This represents 69.2% of the total sales volume. In addition to commercial mixtures, a very small amount—probably not more than a few thousand tons—was home-mixed on the farm. The practice of home mixing, however, has steadily declined because of its inconvenience, questionable thoroughness of mixing, and lack of suitable equipment. Figure 19 shows the location of the fertilizer industry in the U.S. in 1949.

### Types of Mixed Fertilizers

Types of common fertilizer grades, together with a statement as to the usage of each, follow. Typical grades are shown in each group with an example of the amounts



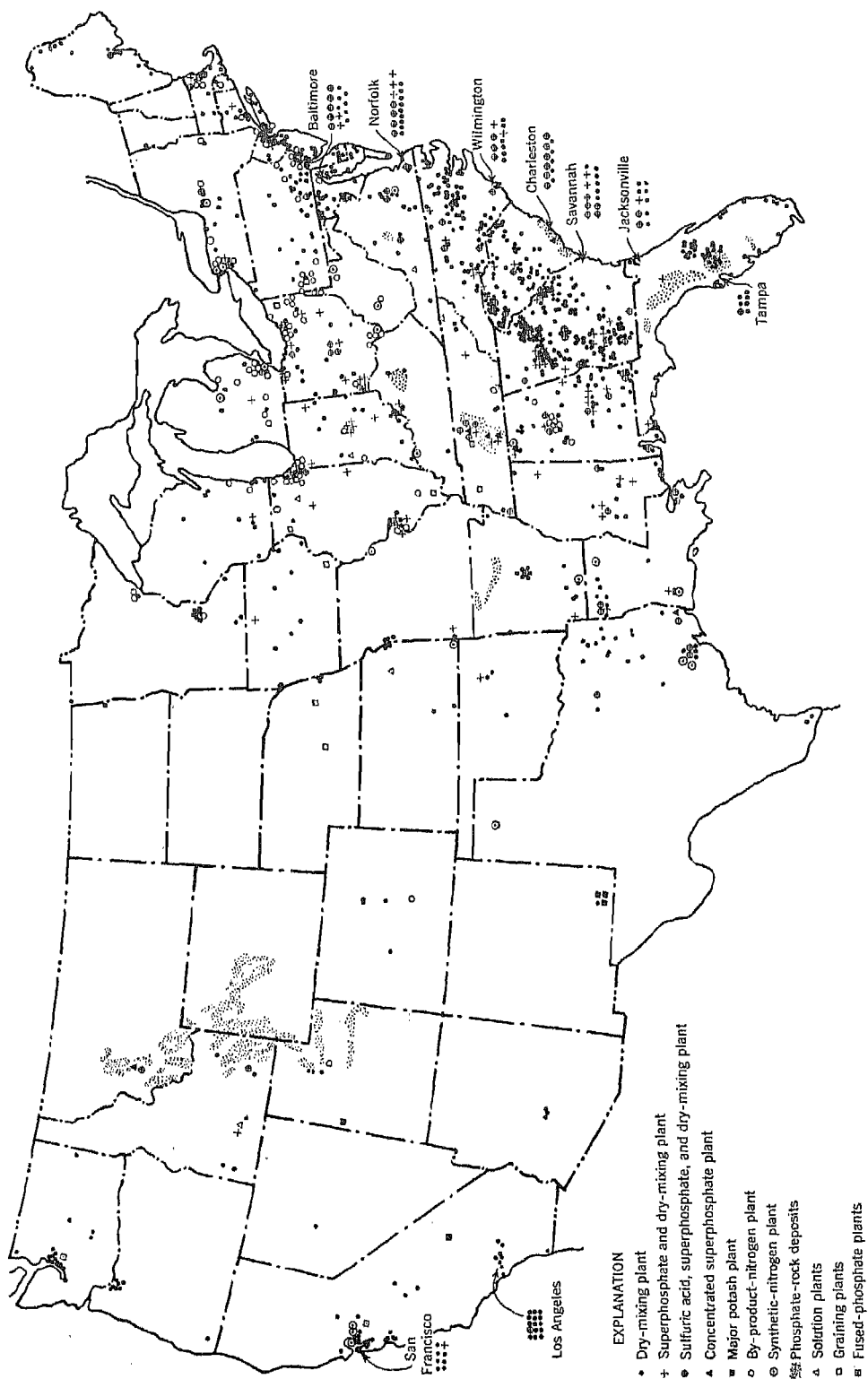


Fig. 19. Location of fertilizer industry in the U.S., 1949.

Courtesy The National Fertilizer Association.

and kinds of raw materials used in formulating one of them. Granular plant foods are usually formulated like regular goods, the granulation being produced by special equipment.

There are many possible formulations of the same grade. The sample formulations shown have been selected at random and are by no means uniformly followed by the industry.

**Nitrogen-Potash.** Mixtures containing nitrogen and potassium only, such as 12-0-12 or 14-0-14, are used mainly as midseason top dressing on sandy soils of the southeastern states. Heavy rainfall and rapid leaching cause a rapid removal of the nitrogen and potassium applied when the crops are planted, though the phosphates largely remain in the root zone. Table XXXI shows a formulation of 12-0-12.

TABLE XXXI. Formulation of 12-0-12 Fertilizer.

Component	Amount, lb.
Ammonium sulfate, 20.5% N.....	1171
Potassium sulfate, 48% K <sub>2</sub> SO <sub>4</sub> .....	500
Finely ground peanut-hull meal (conditioner).....	75
Dolomite.....	254
<i>Total</i> .....	2000

**Nitrogen-Phosphoric Acid-Potash.** Plant-food mixtures containing all three major elements are innumerable. Known as "complete goods" they are used on a variety of crops under a wide variety of soil and climatic conditions. The most common ratios together with an ordinary and high-analysis grade typical of each ratio are given in Table XXXII. Low-analysis grades such as 2-12-6, 3-12-6, 4-8-8, and 3-9-6 of necessity comprised a large tonnage during and for a few years after World War II, since, due to raw-materials shortages, it was necessary to give available materials the widest distribution. With increasing supplies of raw materials such analyses should disappear in favor of the higher grades.

TABLE XXXII. Common Ratios and Examples of Nitrogen-Phosphoric Acid-Potash Fertilizers.

Ratio	Grade	
	Ordinary	High-analysis
1-6-3.....	2-12-6.....	{ 3-18-9 4-24-12
1-4-2.....	3-12-6.....	{ 4-16-8 5-20-10
1-2-2.....	{ 4-8-8 5-10-10	8-16-16
1-2-1.....	5-10-5.....	10-20-10
1-3-2.....	{ 3-9-6 4-12-8	—
1-4-4.....	3-12-12.....	4-16-16
1-1-1.....	7-7-7.....	{ 10-10-10 12-12-12

In some states in addition to total nitrogen, the water-insoluble and nitrate nitrogen guarantee is also required.

TABLE XXXIII. Equivalent Acidity or Basicity of Fertilizer Materials.

Materials	Nitrogen, %	Equivalent acidity or basicity, lb. $\text{CaCO}_3^a$	
		Per unit of nitrogen	Per 100 lb. of product
<i>Nitrogen Compounds</i>			
Ammonium nitrate	33.5	36	60
Ammonium sulfate	20.5	107	110
Ammonium phosphate	11.0	107	59
Ammonium phosphate sulfate	16.5	107	88
A-N-L (or Cal-Nitro)	20.5	0	0
Cyanamid	22	57B	63B
Nitrate of soda potash	14	36B	25B
Potassium nitrate	13	36B	23B
Sodium nitrate	16	36B	20B
Uranon	42	36	75
<i>Ammoniating solutions</i>			
Ammoniating solution I	40.6	36	73
Ammoniating solution II	40.8	36	73
Ammoniating solution III	37.0	36	67
Anhydrous ammonia	82.2	36	148
B-liquor	24.7	36	45
Urea-ammonia liquor A	45.5	36	82
Urea-ammonia liquor B	45.5	36	82
Urea-ammonia liquor C	37.0	36	67
Urea-ammonia liquor D	37.0	36	67
Urea-ammonia liquor 37	37.0	36	67
<i>Natural Organics</i>			
Castor pomace	5.5	19	6
Cacao-shell meal	2.5	10-10B	2-2B
Cottonseed meal	2.0	312B	31B
Milorganite	7.0	29	10
Peanut hulls	0.4	175B	3B
Tankage, animal	6-10	30-30B	15-12B
Tankage, garbage	2.5	50B	7B
Tankage, nitrogenous or process	9.0	34	16
Tobacco stems (processed)	1.7	300B	25B
<i>Phosphates</i>			
Superphosphate	---	---	0
Triple superphosphate	---	---	0
Rock phosphate	---	---	10B
<i>Potash salts</i>			
Manure salts	} Neutral, non-acid-forming	}	
Potassium chloride			
Potassium sulfate			
Sulfate of potash magnesia			
<i>Miscellaneous materials</i>			
Dolomite limestone	---	---	90-100B
Calcium limestone	---	---	80-95B
Hydrated lime	---	---	105-125B
Calcined dolomite	---	---	95-110B
Magnesium oxide	---	---	225-250B
Gypsum (land plaster), kieserite, copper sulfate and manganese sulfate	---	---	Neutral, non-acid-forming
Borax	---	---	50-50B

<sup>a</sup> "B" indicates equivalent basicity instead of equivalent acidity.

Ordinary nitrogen-phosphoric acid-potash grades may be formulated either as "acid-forming" or "non-acid-forming" goods. Certain fertilizer materials, although neutral in reaction themselves, have long been known to change the reaction of the soil to which they are applied. They are termed "physiologically acid" or "physiologically basic."

Most ammonium salts and most organic nitrogen raw materials are physiologically acid. Ammonium salts are acid by hydrolysis. Furthermore, nitrification by soil organisms converts ammonia to nitric acid. By this mechanism, even ammonia is physiologically acid. Other materials such as sodium and calcium nitrates are physiologically basic, since as the nitrate ions are absorbed by the plant, a certain amount of alkaline residue remains in the soil. Details of analytical methods for determining the potential acidity or basicity of fertilizer mixtures are given in reference (1).

The physiological acidity or basicity developed in the soil by plant foods is expressed as pounds of  $\text{CaCO}_3$  per unit (20 lb.) of plant food, equivalent to the base produced or sufficient to neutralize the acid produced. Table XXXIII shows equivalent acidity or basicity figures worked out according to a method developed by Pierre (48).

The acid-forming properties of mixed plant food are particularly important on soils where the use of agricultural limestone is not ordinarily practiced. In Virginia, Alabama, and Mississippi, fertilizer laws require a statement included in the guarantee showing whether the mixture is acid-forming or non-acid-forming, while North Carolina, New York, and South Carolina require a statement as to the potential acidity or basicity in terms of pounds of  $\text{CaCO}_3$  equivalent per ton. Where lime is regularly applied to acid or alkaline soils, the acid-forming properties of plant food are not important. In order to neutralize physiological acidity, non-acid-forming plant foods are formulated to contain enough dolomite so that acid produced by hydrolysis and action of soil bacteria are neutralized.

High-calcium limestone is not desirable since it tends to revert available phosphoric acid to an ammonium citrate-insoluble form. Ordinary fertilizer grades are easily made non-acid-forming. However, there is little or no "room" in the formula of high-analysis mixtures to include sufficient neutralizing material. Use of high-analysis grades on acid soils therefore makes mandatory the practice of liming as a part of regular soil management.

Sample formulations of an ordinary acid-forming, an ordinary non-acid-forming, and a high-analysis acid-forming mixture are shown in Table XXXIV.

TABLE XXXIV. Sample Formulations of 6-12-6 and 10-20-10 Fertilizer Mixtures.

Component	Mixture		
	6-12-6 acid-forming	6-12-6 non-acid-forming	10-20-10 acid-forming
Ammoniating solution, 40.8% N, lb.....	140	140	230
Ammonium sulfate, 20.5% N, lb.....	306	306	181
Ammonium nitrate, 32% N, lb.....	—	—	216
Superphosphate, 19% $\text{P}_2\text{O}_5$ , lb.....	1263	486	—
Triple superphosphate, 45% $\text{P}_2\text{O}_5$ , lb.....	—	328	880
Potassium chloride, 60% $\text{K}_2\text{O}$ , lb.....	200	200	334
Peanut-hull meal (conditioner), lb.....	91	100	150
Dolomite.....	—	440	—
<i>Total</i> .....	2000	2000	2000

**Nitrogen-Phosphoric Acid-Potash-Magnesium (Maximum Chlorine, Nitrate Nitrogen, and Water-Insoluble Nitrogen Guarantee).** This group of plant foods is used principally within the tobacco section of the southeastern states. They usually are formulated according to the recommendation of the Tobacco Research Committee composed of tobacco specialists in the U. S. Department of Agriculture and the Virginia and North Carolina Experiment Stations. It is believed by some workers that more than a small amount of chlorine is detrimental to the burning quality. It is also thought that a certain amount of water-insoluble nitrogen is beneficial in permitting a slower release of this nutrient. Nitrate nitrogen in the amount of 25% of the total nitrogen is also guaranteed. Table XXXV shows a formulation of 4-12-8 with 35% water-insoluble nitrogen, 25% nitrate nitrogen, 2% magnesia, and 2% maximum chlorine.

TABLE XXXV. Formulation of 4-12-8 Fertilizer.

Component	Amount, lb.
Tankage, 8.5% N.....	170
Soybean meal, 7.0% N.....	200
Ammonium nitrate, 32% N.....	125
Aqua ammonia, 24.6% N.....	50
Superphosphate, 19% (av.) $P_2O_5$ .....	846
Triple superphosphate, 45% (av.) $P_2O_5$ .....	176
Sulfate of potash magnesia, 22.5% $K_2O$ , 18.5% $MgO$ .....	216
Potassium sulfate.....	157
Potassium chloride.....	60
<i>Total</i> .....	2000

**Nitrogen-Phosphoric Acid-Potash-Magnesium-Manganese-Copper (Nitrate Nitrogen and Water-Insoluble Nitrogen Guarantee).** Grades guaranteeing six elements are extensively used in Florida where the soils are highly deficient in the minor elements. Included are such grades as 6-8-8-3-2-1. Numerals indicate guaranteed percentages of N,  $P_2O_5$ ,  $K_2O$ ,  $MgO$ ,  $MnO$ , and  $CuO$ , respectively. Table XXXVI shows a formulation of 6-8-8-2-1.5-0.75 with 15% water-insoluble nitrogen, and 10% nitrate nitrogen.

TABLE XXXVI. Formulation of 6-8-8-2-1.5-0.75 Fertilizer.

Component	Amount, lb.
Castor pomace, 6% N.....	300
Ammoniating solution, 40.6% N (11.37% nitrate nitrogen).....	110
Ammonium sulfate, 20.5% N.....	280
Superphosphate, 19% $P_2O_5$ .....	684
Triple superphosphate, 45% $P_2O_5$ .....	67
Potassium chloride, 60% $K_2O$ .....	267
Kieserite, 30.5% $MgO$ .....	132
Manganese sulfate, 28% $MnO$ .....	110
Copper sulfate, 31% $CuO$ .....	50
<i>Total</i> .....	2000

**Specialty Plant Food for Nonfarm Use.** These mixtures are complete plant foods sold in standard and small packages and having a guaranteed analysis such as 6-10-4,

5-10-5, or 10-6-4, together with added minor elements usually not included in the guarantee. Designed for home use on lawns, gardens, and flower beds, these mixtures are generally known to the public under a registered trade name rather than by their guaranteed analysis. In tablet form they are used to feed potted house plants.

**All-Water-Soluble Mixtures.** These are high-analysis mixtures formulated from pure salts which completely dissolve in water leaving no residue. When vegetables are transplanted on commercial truck farms, after being started in the beds, cold frames, or greenhouses, it is a common practice to place either water or a "starter solution" in the hole as each plant is set. All-water-soluble mixtures find use in making up such starter solutions, as well as in liquid-plant-food applications on golf greens and in greenhouses. Two common analyses are 10-52-17 and 15-30-15. An example of a formulation of 1 ton of 10-52-17 is: diammonium phosphate,  $(\text{NH}_4)_2\text{HPO}_4$ , 1000 lb.; and monopotassium phosphate,  $\text{KH}_2\text{PO}_4$ , 1000 lb.

### Equipment Used for Manufacturing Mixed Fertilizers

With the decreased labor supply during World War II and the general trend toward fewer working hours per man, greatly increased mechanization became a necessity. The amount of manual labor per ton of finished product decreased greatly (58). The principal steps are: handling of raw materials, mixing, curing and storage, and bagging and shipping.

The large tonnage of incoming raw materials, arriving principally in freight and tank cars, has to be unloaded and stored for use. Mechanically operated units have replaced most of the hand labor in unloading box cars. Belt conveyors, mechanical unloaders, dump trucks, and overhead cranes now convey most of the raw material to storage. Similarly, when raw materials are made into mixed goods, mechanical devices such as draglines, cranes, dump trucks, and loaders replace much of the hand labor used formerly. See *Conveying*.

In the manufacture of mixed goods, raw materials containing nitrogen, phosphorus, and potassium compounds, as well as dolomite and materials containing the so-called minor elements, are mixed and conveyed to storage for "curing." Batches of one or two or more tons are mixed in each charge. The ingredients in each batch have to be weighed. Instead of man-propelled push carts carrying many small batches over a small scale for weighing, now much larger power-operated trucks go over large, easily read dial scales. In many cases, even these scales have been superseded by a series of batching scales which receive their materials to be weighed from overhead storage hoppers. The storage hoppers are charged by draglines, cranes, loaders, etc. The weighed charge in each batching hopper is discharged through a valve onto a belt conveyor or drag chain, which takes the raw materials to an elevator. The elevator discharges the raw materials onto vibrating screens. The undersize goes into the mixer hopper. The oversize is disintegrated with hammer mills or roll crushers and is recycled to the screen and added to the charge in the hopper. From there the raw material is discharged into a rotary mixer which is usually a baffle shell rotating on a horizontal axis. In larger plants mixers of two or more tons capacity are in use. Situated near the mixer are one or more ammoniating-solution measuring tanks. To each charge definite quantities of these solutions are added in the mixer.

In a comparatively simple plant, the raw materials are taken from separate storage piles by tractors which go over a dial scale for proper weighing of each charge.

The raw materials are discharged into an elevator (See Fig. 20) which discharges onto a vibrating screen. The undersize is stored in a hopper ahead of the mixer and the oversize passes through the hammer mill or roll crusher and is recycled to the vibrating screen. The hopper is discharged into a mixer in which solids are mixed and ammoniating solution is then added. The mixer charge is taken to storage for curing.

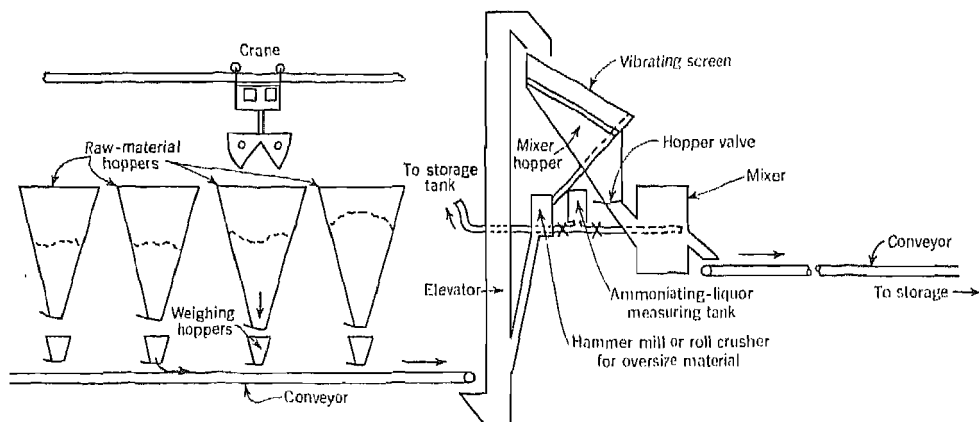


Fig. 20. Crane-type mixing plant.

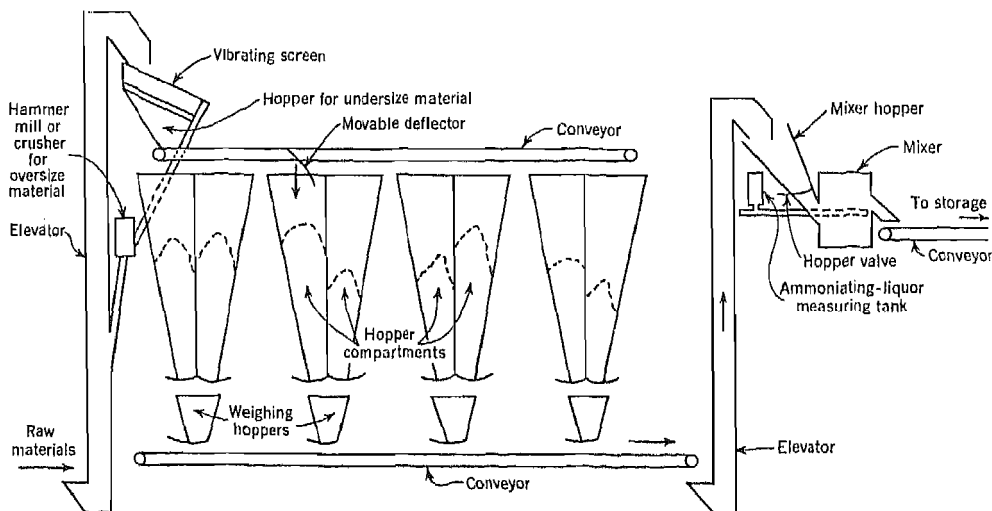


Fig. 21. Two-elevator mixing unit.

Figure 20 shows the crane-operated plant. The raw materials are put in the hoppers by means of overhead cranes. Below each raw-materials hopper is a scale hopper in which the raw materials are weighed. From there the raw materials are discharged into an elevator, and are screened and mixed. Ammoniating solutions are added in the mixer. The mixer discharge can be carried by belt conveyors to temporary storage or to storage for curing.

Figure 21 is a two-elevator mixing unit. The raw materials are elevated to a vibrating screen. The oversize is disintegrated and recycled to the screen. The hopper below the screen discharges on a belt conveyor, which discharges into hoppers.

Each hopper has two compartments. Each raw material is discharged into the desired compartment by means of a movable deflector on the belt conveyor. Below each hopper is a scale hopper which receives two materials from the two compartments above it. The scale hoppers are discharged on a belt conveyor which discharges into another elevator which feeds a rotary mixer, where the solids are thoroughly mixed and ammoniated. The mixer discharge is taken to storage by belt conveyors or overhead dump trucks.

Figure 22 shows a unique mixing scheme developed by Chemical Engineering Service at Green Bay, Wisconsin. The raw materials are weighed automatically. Predetermined amounts of various ingredients are automatically charged into a weighing hopper by means of Syntrol vibrating feeders from raw-materials storage hoppers.

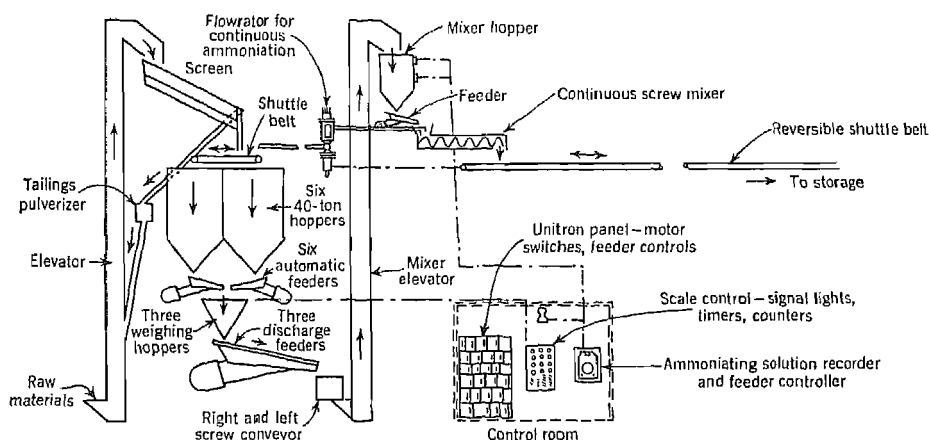


Fig. 22. Automatic mixing plant.

After the proper amount of each ingredient desired has been delivered to the weighing hoppers, electronic devices in the control room automatically discharge the weighing hoppers with Syntrol feeders into a screw conveyor which delivers the charge to an elevator. The elevator discharge goes into a mixer hopper in which the solids are mixed. The contents of the mixer hopper are continuously discharged at a predetermined rate by the Syntrol feeder which discharges into a continuous screw mixer in which predetermined amounts of ammoniating solutions are continuously added. The product of the continuous screw mixer is continuously delivered to a reversible shuttle belt which conveys the mixed goods to storage for curing.

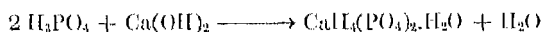
### Changes in Physical and Chemical Properties

Chemical reactions usually occur in the manufacture of mixed fertilizers. The products formed may have improved physical and chemical properties or the opposite may be the case. Reactions may be instantaneous or may require months for completion. They may be accompanied by a sharp rise in temperature and may even cause spontaneous combustion or toxic gases may be liberated. The reactions can affect the hygroscopicity of the products formed and influence the drillability in the farmer's distributing machinery. The resultant product may be dusty or the fine particles may agglomerate to granular, free-flowing material. The reaction products may

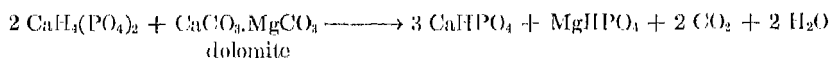
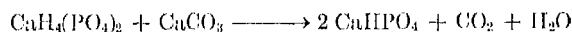


have less desirable chemical properties or they may be improved and be better sources of plant nutrients than the original materials.

Liming materials such as finely ground dolomite, calcium carbonate, calcium hydroxide, or calcium magnesium oxide are frequently used in fertilizers containing a mixture of superphosphate and potash salts (for example, 0-14-14), ordinary superphosphate (for example, 0-20-0), or triple superphosphate (for example, 0-45-0). The liming material reacts with the free phosphoric acid in the superphosphate:

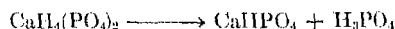


Quantities of liming materials larger than the amount necessary to neutralize the free phosphoric acid, react to form:



Dicalcium phosphate,  $\text{CaHPO}_4$ , can take up 2 moles of water; magnesium phosphate can form hydrates with 3 and 7 moles of water. Dolomite is preferable to calcium carbonate since high-calcic limestone may change some dicalcium phosphate to tricalcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , which is only partially ammonium citrate-soluble.

If just enough liming material is added to superphosphate to neutralize the free acid, the resulting product shows a reduction in free acid but not complete disappearance of it. This is due to subsequent hydrolysis:



From 60 to 100 lb. of finely ground limestone and occasionally even larger amounts are added per ton of phosphate-potash mixtures or straight superphosphate. The reaction is very slow and as it progresses (cures) the product hardens and cakes. The caked material is put through a hammer mill, screened, bagged, and then is ready to be shipped. The product is now less hygroscopic and more free-flowing.

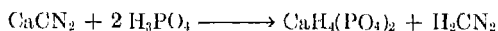
In unlimed superphosphate there is some free hydrofluoric acid and in unlimed phosphate potash mixtures containing potassium chloride, hydrochloric acid is formed in addition to hydrofluoric. These volatile acids cause deterioration of cotton and burlap bags. High temperatures prevailing in summer in closed box cars or warehouses greatly accelerate bag rot. Liming of the superphosphate reduces the free phosphoric acid and this in turn prevents liberation of hydrochloric and hydrofluoric acids. If instead of ground limestone, hydrated lime, calcined limestone, or magnesium oxide is used, the curing time is reduced. Excessive amounts of these materials convert some of the ammonium citrate-soluble and available phosphoric acid to ammonium citrate-insoluble and unavailable phosphoric acid.

In the decomposition of carbonates of calcium and magnesium in superphosphate, carbon dioxide is liberated. Since carbon dioxide is heavier than air, it should not be permitted to accumulate in enclosed and poorly ventilated space near the storage pile. A few fatal accidents have occurred under such conditions. With relatively high concentrations of carbon dioxide, death apparently occurred much more rapidly than could be ascribed to mere oxygen deficiency.

Borax and its partially dehydrated salts are used in plant-nutrient mixtures containing superphosphate and potassium chloride. The addition of relatively small amounts, about 40 lb. per ton or less, is beneficial; larger amounts are detrimental to

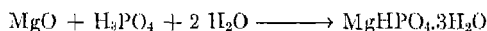
the physical condition of the mixture. The beneficial effect of small amounts is due to neutralization of free phosphoric acid with borax. Larger amounts make the product more hygroscopic because of the formation of monosodium phosphate.

Cyanamid (calcium cyanamide) reacts rapidly with free phosphoric acid and monocalcium phosphate in superphosphate. The free lime present as an impurity and the highly reactive calcium cyanamide decrease the free acid and improve the physical condition of the superphosphate:



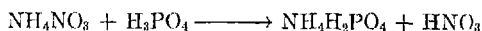
The free cyanamide produced forms a series of compounds which include urea and ammonia. Excessive amounts of cyanamide cause reversion of phosphates to an ammonium citrate - insoluble form.

Magnesium oxide obtained from sea water readily reacts with free phosphoric acid and monocalcium phosphate. When about 40 lb. per ton of sea-water magnesium oxide is added to ordinary superphosphate, triple superphosphate, or phosphate potash mixtures, neutralization is rapid, heat is liberated, and the product becomes less hygroscopic, is more free-flowing, and has less tendency to cake after curing:

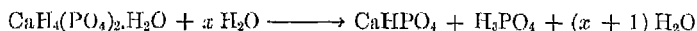


Some calcined magnesium oxide, obtained by heating magnesite,  $\text{MgCO}_3$ , and driving off carbon dioxide, is less reactive than that obtained from sea water. With it most of the liberation of heat takes place after the product is put in storage for curing. Some reversion of citrate-soluble phosphate to the citrate-insoluble form may result. The product also tends to harden considerably in storage.

Inorganic nitrates when present in large amounts may cause spontaneous combustion in fertilizer mixtures containing superphosphate and organic matter. The excessive development of heat is the result of oxidation of organic matter by nitric acid, which is formed in the reaction between the nitrate and free phosphoric acid in superphosphate:



The rate of reaction is accelerated by increasing the concentration of free phosphoric acid in the liquid phase of the fertilizer. A rise in temperature will increase the degree of hydrolysis of monocalcium phosphate (see Fig. 23).



Combustion in curing piles is a rare occurrence, an indication that conditions seldom exist that permit the reaction to develop sufficient heat to ignite the combustible material present. However, a prolonged high temperature in the curing pile is frequently observed, especially with high-analysis mixtures. This condition may and often does result in the loss of available plant food, either by decomposition of

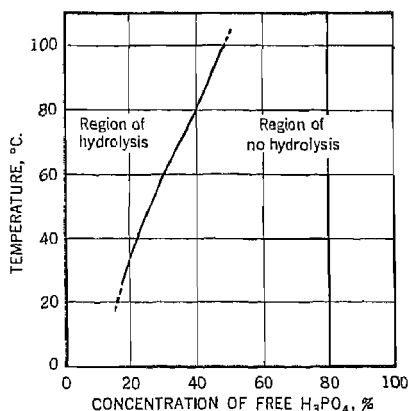


Fig. 23. Effect of temperature on hydrolysis of monocalcium phosphate to dicalcium phosphate and free  $\text{H}_3\text{PO}_4$  (16).

nitrogenous compounds to cause loss of nitrogen, or by the reversion of phosphate to less available forms. See Table XXXVII (16).

TABLE XXXVII. Composition of Base Mixture Before and After Storage at Different Temperatures.

Composition	Original mixture	Storage temp., °C.	
		30	85
Storage time.....	—	4 weeks	2 hr. <sup>a</sup>
Water, %.....	3.97	3.71	3.62
Nitrogen, %.....	6.70	6.71	6.16
Phosphoric acid, P <sub>2</sub> O <sub>5</sub> , %			
Water-soluble.....	28.32	28.44	24.57
Citrate-soluble.....	None	0.04	0.04
Free.....	1.17	1.17	7.28 <sup>b</sup>
Total.....	32.78	33.09	35.55
CaH <sub>4</sub> (PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O, %.....	27.15	27.27	17.25
CaHPO <sub>4</sub> , %.....	4.46	4.61	10.98
H <sub>3</sub> PO <sub>4</sub> , %.....	1.61	1.61	10.06
H <sub>3</sub> PO <sub>4</sub> /(H <sub>3</sub> PO <sub>4</sub> + H <sub>2</sub> O), %.....	28.9	30.3	73.5

<sup>a</sup> After 2 hours at 85°C., it was necessary to cool the mixture rapidly to prevent ignition.

<sup>b</sup> Based on the original free acid plus that calculated from the decrease in water-soluble phosphoric acid.

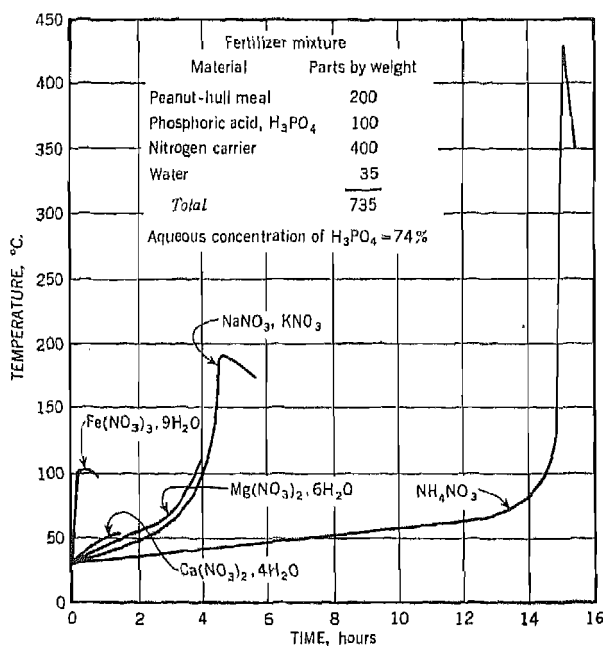
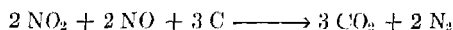


Fig. 24. Effect of different nitrates on heat development in stored fertilizer mixture (16).

The reaction between nitric acid and many forms of oxidizable organic matter occurs readily at low temperature to form water, carbon dioxide, and the various oxides of nitrogen. During complete combustion in the presence of sufficient car-

bonaceous matter, the oxides of nitrogen may react further to form carbon dioxide and elemental nitrogen:



The use of as little as 50 lb. of peanut-hull meal per ton of mixture may be sufficient to cause combustion under certain conditions. Most of the vegetable-seed meals, animal meals, sewage sludge, garbage tankage, kraft paper, and other materials used frequently as conditioners may ignite spontaneously under certain conditions.

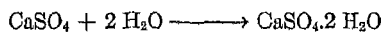
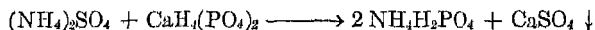
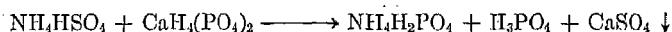
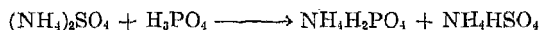
At temperatures below 90°C., the reaction is similar for all inorganic nitrates ordinarily used in fertilizer mixtures. Above 90°C. the reaction involving ammonium nitrate is many times more rapid than that involving either sodium or potassium nitrate. Figure 24 shows the effect of different nitrates on heat development in a mixture stored at 30°C. The mixture contained the equivalent of 100 lb. of free phosphoric acid, 400 lb. of nitrogen carrier, 200 lb. of peanut-hull meal, and 35 lb. of water per batch of 735 lb. The remaining 1265 pounds of inactive material required to complete the formula on the ton basis were omitted from the test batches in order to eliminate the blanketing effect of dilution on the heat developed in such a small test sample. The nitrogen carriers used were ammonium, potassium, and sodium nitrates, calcium nitrate tetrahydrate, magnesium nitrate hexahydrate, and ferric nitrate containing approximately 9 molecules of water of crystallization. The greatly accelerated rate of chemical reaction at 90–100°C., which causes extremely rapid combustion to occur in the mixture containing ammonium nitrate, is not evident in any of the mixtures containing other nitrates. After completion of the reaction, the organic matter in the mixture containing either sodium or potassium nitrate was slightly charred but that in the mixture containing ammonium nitrate was converted to ash.

Spontaneous combustion can be prevented by the addition of a rapid neutralizing agent such as ammonia, in sufficient quantity to convert free  $\text{H}_3\text{PO}_4$  in superphosphate to  $\text{NH}_4\text{H}_2\text{PO}_4$ , and  $\text{CaH}_4(\text{PO}_4)_2$  to  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{CaHPO}_4$ . This prevents the formation of large quantities of nitric acid.

At lower temperatures (30°C.), however, it is necessary to neutralize only the free acid present in the superphosphate, since it was shown in Figure 23 that hydrolysis does not occur at this temperature to produce free phosphoric acid in concentrations greater than 19%. However, care must be exercised to prevent a prolonged high temperature from developing. This can be accomplished by cooling the mixture and by building up the storage piles slowly. Neutralizing agents such as ground limestone and ground dolomite react too slowly with phosphoric acid to prevent the formation of nitric acid.

Even though no organic matter is added to a mixture of inorganic nitrates and superphosphate which has not been neutralized, the nitric acid formed will be reduced to nitrogen oxides by the organic matter naturally present in most superphosphate. The gases liberated can be a health hazard and in extreme cases may prove fatal to man.

Ammonium sulfate reacts with the free acid and monocalcium phosphate in superphosphate to form the following principal products:



The reactions which take place cause the fertilizer mixture to harden during the curing process. Before it is ready to be disintegrated, screened, and shipped, the reactions should be near completion.

When relatively well-cured and dry superphosphate is mixed with ammonium sulfate, the reaction proceeds slowly and may require 2 months or more. In the early stages the product becomes more moist and free water appears to be liberated. This may be due to the moisture set free during the decomposition of hydrated monocalcium phosphate. Later, however, the free moisture is reduced. The calcium sulfate formed probably changes into the hemi- and dihydrates.

Potassium sulfate, in reacting with superphosphate, behaves much the same as ammonium sulfate, forming  $\text{KH}_2\text{PO}_4$ . The resultant product becomes extremely hard during curing. However, after the reaction is completed, it is in excellent physical condition. A double salt of calcium sulfate and potassium sulfate may be formed,  $\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (syngenite).

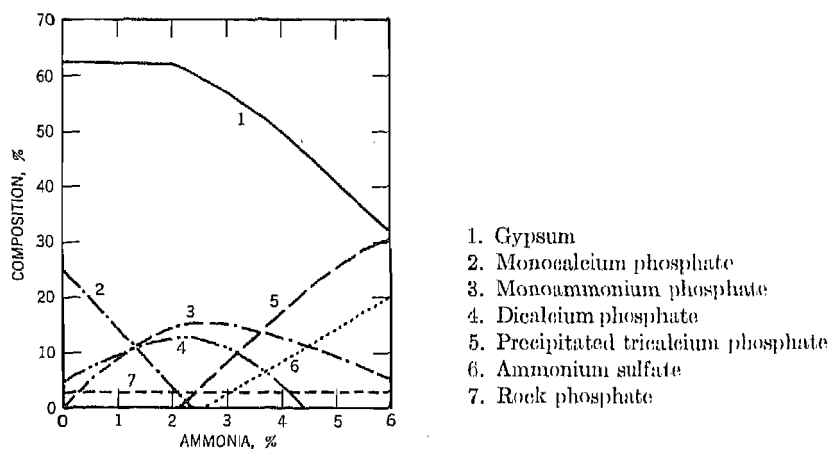


Fig. 25. Change in composition of superphosphate caused by ammoniation (30).

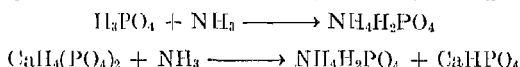
Anhydrous magnesium sulfate (kieserite),  $\text{MgSO}_4$ , and  $\text{CaH}_4(\text{PO}_4)_2$  form  $\text{MgHPO}_4$  and calcium sulfate. Considerable heat is liberated. The  $\text{MgHPO}_4$  can take up 3 and 7 moles water of crystallization. The product becomes hard in cure.

Hydrated magnesium sulfate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , forms products similar to kieserite; however, there is no marked increase in temperature. The magnesium phosphate formed is soluble in ammonium citrate solution and the phosphate is available according to the standards of the A.O.A.C.

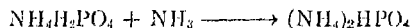
Copper, zinc, and manganese sulfates used in plant-food mixtures form their less soluble phosphates when mixed with superphosphates. Their chemical composition is not definitely known. The products formed are soluble in ammonium citrate solution. If relatively large amounts of zinc, copper, and manganese sulfates are added to superphosphates and the mixture is treated with ammonium hydroxide or anhydrous ammonia, some of the phosphate becomes insoluble in ammonium citrate solution. It is conceivable that apatite-like compounds are formed with zinc, copper, and manganese.

Ammoniating solutions react with superphosphate to form a series of compounds depending on the amount of uncombined ammonia used. The reaction of uncombined ammonia with the acidic components of superphosphate is almost instantaneous as contrasted with the slow reaction of ammonium sulfate, potassium sulfate, and other sulfates.

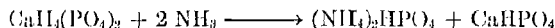
The principal reaction is the neutralization of free acid and conversion of water-soluble monocalcium phosphate into water-insoluble but ammonium citrate-soluble dicalcium phosphate plus monoammonium phosphate. (See Fig. 25.)



The addition of two moles of free ammonia per mole of water-soluble phosphoric acid converts the monoammonium phosphate into diammonium phosphate if the temperature is kept below 75°C. Diammonium phosphate decomposes above 75°C.



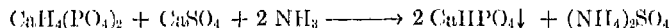
This reaction may also be carried on at higher temperatures under pressure to prevent decomposition of the diammonium phosphate. Combining the last two equations gives:



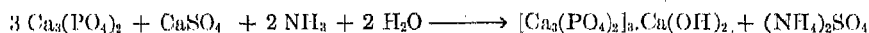
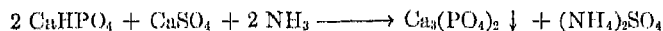
The presence of about two moles of calcium sulfate per mole of monocalcium phosphate in ordinary superphosphate has little influence on the chemical reaction in the first stage of ammoniation. One mole of neutralizing ammonia is quickly absorbed per mole of monocalcium phosphate. This is equivalent to 2.4 lb. of neutralizing ammonia to approximately 100 lb. of 20% superphosphate. Triple superphosphate, which is mostly monocalcium phosphate, reacts with two moles of ammonia to form diammonium phosphate. In ordinary superphosphate the diammonium phosphate formed reacts quickly with calcium sulfate:



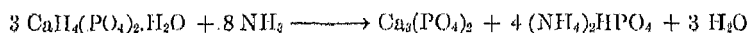
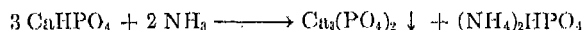
If no additional reactions occurred the sum of the last two reactions would be:



There are indications that while the last reaction takes place, the dicalcium phosphate formed reacts simultaneously with more ammonia to form tricalcium phosphate (see Fig. 25). Some of the tricalcium phosphate is converted into calcium hydroxyphosphate and calcium fluorophosphate,  $[\text{Ca}_3(\text{PO}_4)_2]_3 \cdot \text{CaF}_2$ . The tricalcium phosphate formed is not completely ammonium citrate-soluble and the calcium hydroxyphosphate is very slightly so.



In triple superphosphate, not containing calcium sulfate, the dicalcium phosphate may react with ammonia as follows (see Fig. 25):



Some tricalcium phosphate is converted into  $[\text{Ca}_3(\text{PO}_4)_2]_3 \cdot \text{Ca}(\text{OH})_2$  and  $[\text{Ca}_3(\text{PO}_4)_2]_3 \cdot \text{CaF}_2$ .

The last four reactions and Figure 25 indicate that excessive amounts of free ammonia cause reversion of available phosphates into insoluble forms. Due to difference in chemical composition of commercial superphosphates, the addition of equivalent amounts of free ammonia to the superphosphate causes different amounts of reversion. See Table XXXVIII.

TABLE XXXVIII. Analyses of Various Commercial Superphosphates Before and After Ammoniation.

Composition	Superphosphate No.							
	1	2	3	4	5	6	7	8
Moisture, %	4.5	7.7	5.9	7.6	8.3	4.5	6.5	7.2
Free $\text{H}_3\text{PO}_4$ , %	1.2	3.5	3.9	3.0	1.0	2.6	2.8	2.9
Total $\text{P}_2\text{O}_5$ , %	19.8	18.2	20.6	21.1	19.1	21.5	19.8	21.2
Citrate-insoluble $\text{P}_2\text{O}_5$	0.39	0.20	0.28	0.45	0.48	0.13	0.48	0.41
Available $\text{P}_2\text{O}_5$	19.4	18.0	20.3	20.6	18.6	21.4	19.3	20.8
Per cent of total $\text{P}_2\text{O}_5$								
available	98.0	98.9	98.6	97.9	97.5	99.4	97.6	98.1
Fluorine, %	1.57	1.68	1.92	1.80	1.70	2.15	1.67	2.07
$\text{FePO}_4$ , %	1.10	1.14	1.16	1.81	0.80	0.91	2.10	1.06
$\text{AlPO}_4$ , %	2.77	1.55	1.99	2.36	1.98	1.43	4.33	1.57
$\text{CaO}$ , %	28.30	30.50	30.35	30.10	29.28	31.13	28.25	30.45
$\text{SO}_3$ , %	27.75	30.55	28.78	28.48	29.20	29.18	30.55	29.35
Mole ratio $\text{SO}_3:\text{CaO}$	0.685	0.701	0.664	0.665	0.698	0.655	0.759	0.674
After ammoniation <sup>a</sup>								
Total nitrogen, %	5.60	4.56	4.59	4.57	5.26	4.58	4.70	4.59
Wt. ratio free $\text{NH}_3$ to total $\text{P}_2\text{O}_5$								
Nominal	0.152	0.165	0.146	0.142	0.158	0.139	0.152	0.141
Found	0.216	0.159	0.139	0.132	0.183	0.128	0.148	0.137
Total $\text{P}_2\text{O}_5$ , %	17.3	16.4	18.5	18.5	17.1	19.2	17.1	19.2
Citrate-insoluble $\text{P}_2\text{O}_5$ , %	0.36	0.27	0.40	0.79	0.32	0.24	0.51	0.61
Citrate-insoluble $\text{P}_2\text{O}_5$ re- verted, %	0.1	0.6	0.8	2.2	0.6	0.7	0.6	1.7

<sup>a</sup> Original superphosphates ammoniated with 30 lb. of free  $\text{NH}_3$  per 1000 lb. superphosphate as prepared.

Source: reference (18).

Increase in temperature accelerates formation of ammonium citrate-insoluble phosphates. The amount of ammonia reacting with superphosphate and the temperature of the superphosphate in the beginning of ammoniation are largely responsible for the temperature of the mass after ammoniation.

The following increases in temperatures in a ton of fertilizer, containing superphosphate, from 1 lb. of neutralizing ammonia are about as follows: anhydrous ammonia, 2.5°F.; ammoniation solutions, consisting of ammonia, water, and ammonium nitrate, or ammonia, water, and urea, 1.70°F.; and aqua ammonia, 1.50°F. The addition of 30 lb. of neutralizing ammonia will increase the temperature approximately 75, 51, and 45°F., respectively.

Table XXXIX (18) shows the reversion of total  $P_2O_5$  of the ammoniated superphosphate as affected by time and temperature of storage and by fluorine content.

TABLE XXXIX. Effect of Time and Temperature on Reversion.

	Superphosphate							
	A	B	C	D	E	F	G	H
Fluorine content, %.....	1.57	1.67	1.68	1.70	1.80	1.92	2.07	2.15
Reversion, %								
At room temp. for 36 days.....	1.1	3.5	1.5	1.1	3.3	2.1	3.1	4.5
At 104°F.								
For 42 days.....	4.1	6.9	5.4	4.2	7.5	4.9	5.9	7.4
For 124 days.....	6.6	9.2	9.3	8.8	9.9	5.9	8.7	8.7
At 122°F.								
For 37 days.....	5.2	8.1	6.6	5.6	8.1	4.9	7.2	8.4
For 121 days.....	7.6	10.1	9.6	9.6	9.9	6.5	8.6	9.8
At 184°F.								
For 27 days.....	7.7	12.0	9.1	16.8	12.0	7.0	9.1	8.9
For 112 days.....	12.6	20.3	14.7	26.1	21.8	11.0	13.7	11.7

The data in Table XXXIX indicate that reversion of total phosphoric acid in ammoniated superphosphate increases with high storage temperature and duration of storage. The amount of fluorine present apparently does not accelerate reversion as much as some investigators held it would.

In factory operations the equipment used may have a bearing on reversion. Over-ammoniation of portions of a mixture no doubt take place. With the kind of equipment used, absolutely uniform distribution of the ammoniating solutions is not achieved. Local excesses of ammonia in the mixture will cause almost simultaneous formation of diacalcium phosphate, tricalcium phosphate, and calcium hydroxyphosphate. Probably very little of the calcium hydroxyphosphate will change back to ammonium citrate--soluble product, although some of the tricalcium phosphate may, under favorable conditions.

### Granulated Fertilizers

Granulated plant foods are in some demand because their low percentages of fines make them somewhat more free-flowing and easily drillable than regular mixed goods. There is less fixation of phosphate from granular goods in soils with high fixing capacities where heavy applications are made. Because of their free-flowing advantage they are in particular demand for aircraft application on rice. However, the granulated fertilizers comprise only a very small percentage of the total sold in the U.S. The present distribution machinery for hand placement does not place granulated plant foods as uniformly as regular goods. The use of ammoniating solutions in mixed goods manufacture makes a naturally more granular product as compared to the dry-mixed fertilizers in England, where granulated goods make up the bulk of the trade. Further, because of the higher production costs, granulated fertilizers demand a premium price.

Fertilizers are made granular by suitable physical treatment. Figure 26 shows the arrangement for a granulated process used by the Davison Chemical Corporation.

To granulate either superphosphate or mixed plant foods requires processing in



two stages. In the first stage, superphosphate or mixed goods (whichever is being processed) is fed into the conditioner, which consists of a rotating cylinder in which the material to be granulated is moistened with sprayed water. An important part of the process is to feed the material from the conditioning cylinder into a revolving drying cylinder at exactly the right degree of granulation and correct moisture content. The operator who exercises the control is stationed at the discharge end of the conditioner and inspects the flood-lighted material as it passes. Control is by manual operation of the valves which feed water into the sprays within the conditioning chamber. In the

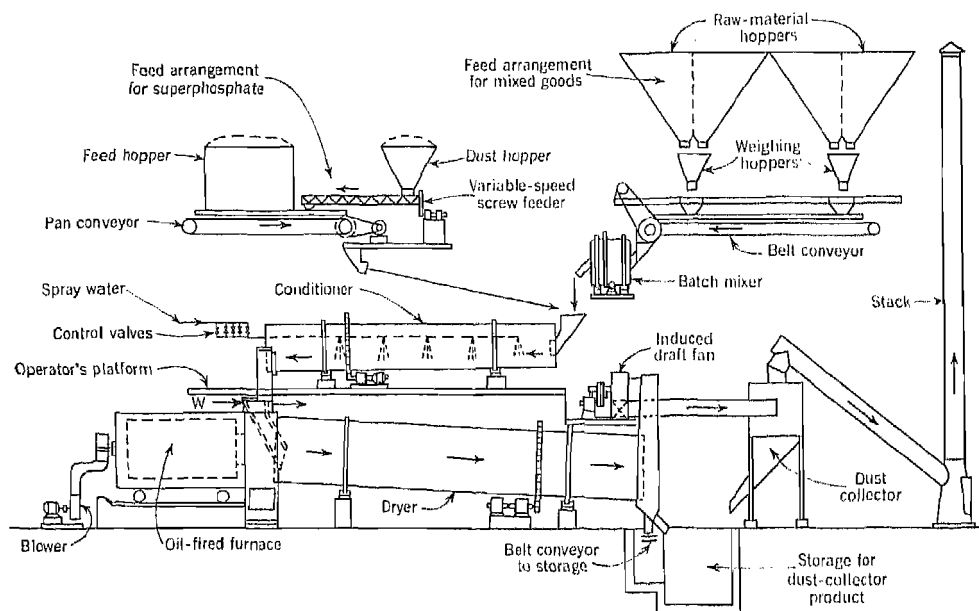


Fig. 26. Fertilizer granulation unit (33).

second stage, the conditioned material discharges at the lower end directly into the feed hopper at the hot end of the dryer. The conditioned material enters at the hot or furnace end through a water-jacketed feed chute and progresses downward to be discharged at the lowest or cool end either onto a belt conveyor which takes it to storage or into a pit from which it is moved by crane to stock piles for cooling and curing prior to screening and shipping. If the freshly granulated material is to be shipped promptly it is usually put through a rotary cooler after leaving the dryer.

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**FIBERBOARD.** See *Plywood and composition boards.*

## FIBERS

The word fiber originally referred only to naturally occurring materials, such as cotton, flax, hemp, wool, hair, and silk, and describes long, thin objects, which, besides their filiform shape, possess considerable tensile strength, toughness, and flexibility. This word is now also used for products of nonnatural origin, such as viscose rayon, and acetate rayon (estron), nylon, Orlon, Vinyon, Saran, aralac, Ardil, and Vicara. Some of these man-made fibers, for example, viscose rayon and the various respun protein fibers such as aralac (from casein), Ardil (from peanuts), and Vicara (from zein (corn protein)), are of a "half-synthetic" character. In these, a natural polymeric material such as cellulose or protein is brought into a dissolved or dispersed state and then spun into fine threads. Others are "full synthetics," such as nylon, Orlon (an acrylic fiber), Vinyon (a vinyl copolymer), and Saran (polyvinylidene chloride). Here a synthetic polymer is first made by a process of polymerization or polycondensation. This polymer is then, from its melt or solution, processed into fiber form. An intermediate state is taken by cellulose acetate rayon, where a natural polymer, cellulose, is first converted into one of its derivatives, cellulose acetate, which is then dissolved and spun into fiber form. The original starting material is, in this case, a naturally occurring polymer, but the final product is chemically different from it and does not occur in nature as such. There exist in nature also fibrous materials of inorganic character, such as asbestos and other silicates, which are put to practical use, and there are many inorganic substances that have been processed into fiber form, such as steel, tantalum, quartz, and glass.

Fibers are of great practical importance. They represent the raw materials for many industrial processes such as spinning, knitting, braiding, and weaving.\* The

**TABLE I. Approximate World Fiber Consumption.**

Fiber	Consumption, millions of pounds			
	1920	1930	1940	1950 <sup>a</sup>
Cotton	8,000	8,000	9,000	11,000
Wool	—	700	800	900
Silk	60	100	120	130
Rayon	—	200	1,100	2,100
Nylon	—	—	—	60
Hemp, jute, flax, and sisal	700	700	800	900

\* Estimated.

**TABLE II. Average Prices of Various Fibers in the U.S., 1950.**

Fiber	Price, \$/lb.	Fiber	Price, \$/lb.
Cotton	0.25-0.35	Wool	1.00-3.00
Viscose rayon staple	0.25-0.30	High-tenacity rayon	1.00-1.50
Flax and hemp	0.30-0.50	Vinyon N yarn	1.20-1.50
Acetate rayon staple	0.35-0.50	Silk	2.00-6.00
Viscose rayon yarn	0.50-0.70	Nylon	2.50-3.50
Acetate rayon yarn	0.55-0.85	Orlon	2.80-3.60
Respun protein	0.65-0.80		

world consumption of all types of fibers is large; Table I contains a few approximate figures of the amount and value of different fibers consumed in 1920, 1930, and 1940, together with the estimated figures for 1950. Table II gives the prices of various fibers. See *Cotton*; *Fibers, vegetable*; *Linen*; *Polyamides*; *Protein fibers, synthetic*; *Rayon*; *Silk*; *Textile fibers, synthetic*; *Textile technology*; *Textile testing*; *Wool*.

### Geometrical and Other Physical Properties

There exist essentially two types of fibers, as far as their *length* and *length distribution* are concerned: *continuous* filaments and *staple* fibers. In the first case (rayon, silk, nylon, Orlon, Vinyon, etc.), the length of the individual fiber is virtually infinite. In the second case (cotton, wool, and artificial staple fibers), it is of the order of magnitude of inches. Artificial staple fibers have a uniform length and are usually cut to filaments between 6 and 20 cm. Cotton and wool exhibit considerable nonuniformity which leads to the necessity of using a length distribution function, the so-called *staple diagram*, for the accurate characterization of a given sample, and to use an average staple length for any preliminary or approximate description of the material.

Figure 1(a) gives the staple diagram of an American cotton having an average length of 1.02 cm., whereas Figure 1(b) shows the staple diagram of a West Australian

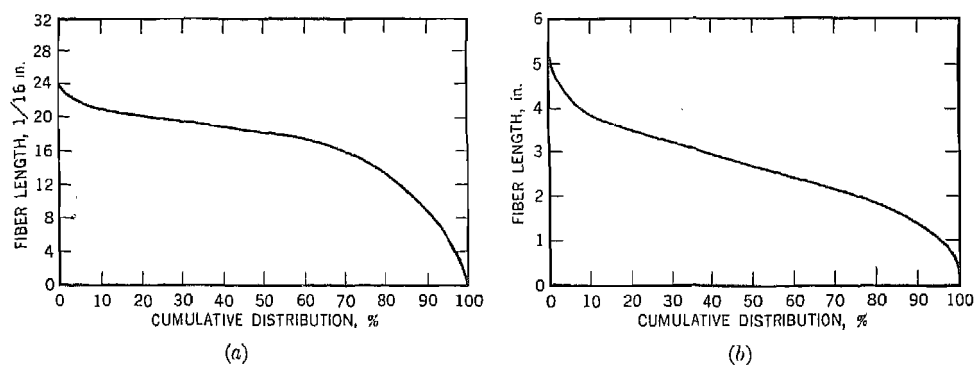


Fig. 1. Staple distribution diagrams: (a) American cotton; (b) West Australian wool. (a, courtesy U.S. Dept. Agr., Production and Marketing Administration; b, courtesy Forstmann Woolen Co.)

wool with an average length of about 2.69 cm. It can be seen that both samples exhibit a considerable heterogeneity as far as the length of the individual fibers is concerned.

In considering the length of a fiber, attention must be given to the existence of *crimp*. Certain fibers such as silk, flax, rayon, and nylon are virtually smooth, even elements which can be laid down as straight, uncurled filaments; others such as cotton and wool have a natural tendency to assume an irregularly undulated shape; others, again, such as rayon, nylon, Orlon, and Vinyon can be treated in various ways so as to develop a more or less permanent crimp. Extent and permanence of the crimp are of great importance for the processibility of staple fibers and for some of the final properties of the yarns and fabrics made from them, particularly for their hand, softness, and warmth.

Another important property of a fiber is the size and shape of its *cross section* and the uniformity of the cross section along its length. In textile technology, cross

sections of fibers are usually not measured directly, but in *denier* or *grex*, which are units proportional to the length having a given weight. A fiber has a cross section corresponding to one denier (one grex) if 9,000 (10,000) meters of it weighs one gram.

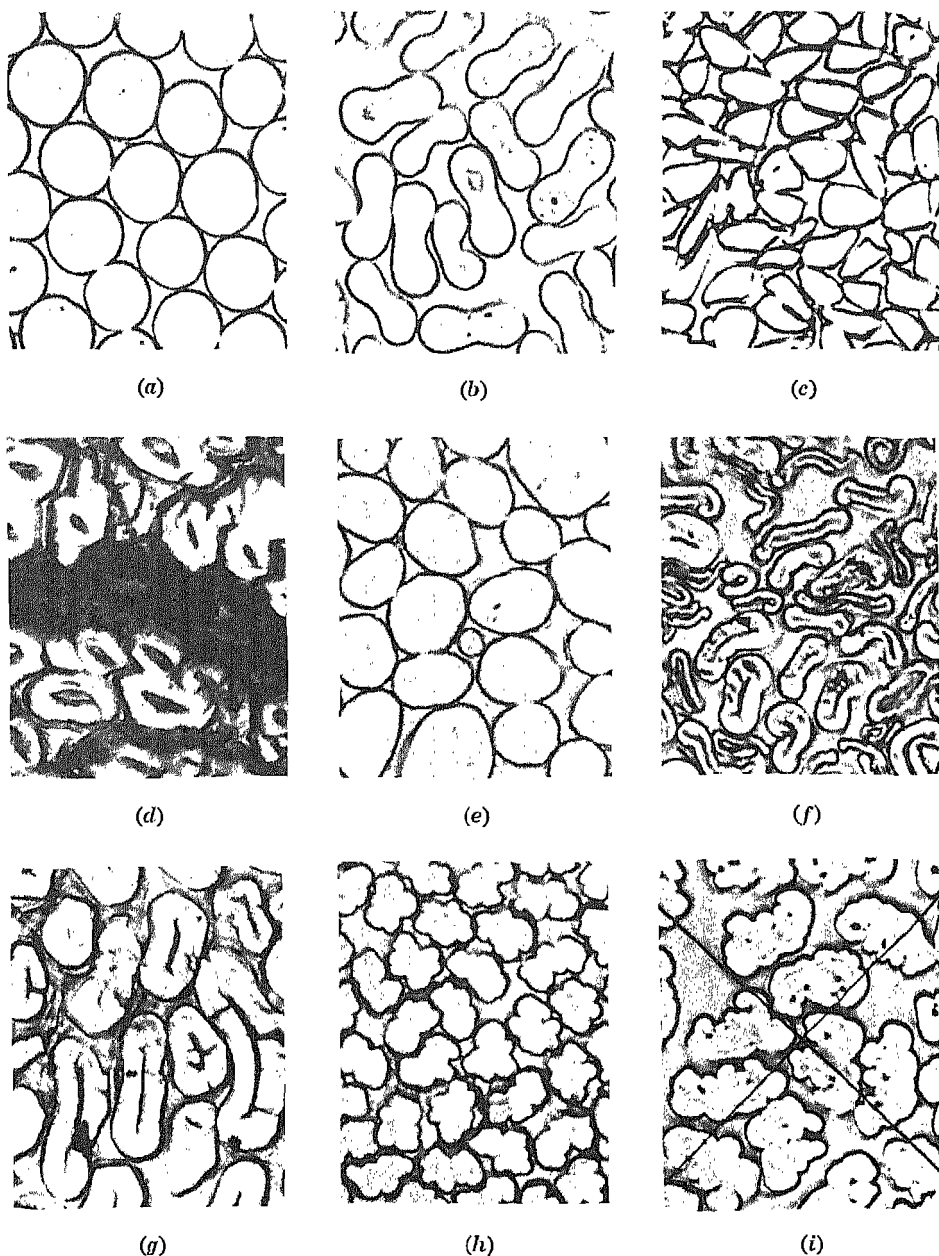


Fig. 2. Cross sections of various fibers ( $\times 500$ ): (a) nylon; (b) Orlon; (c) silk; (d) unretted seed flax; (e) wool; (f) Empire cotton; (g) ramie; (h) acetate rayon; (i) high-tenacity viscose rayon (a-h, courtesy U.S. Dept. Agr., Southern Regional Research Laboratory; i, courtesy E. I. du Pont de Nemours & Company).

As a consequence of this definition the denier or grex of a fiber or yarn depends upon its specific gravity and cannot be used for direct comparison of samples having noticeably different densities.

A few fibers, such as nylon and certain rayons, have almost circular cross sections with a smooth surface. Silk is roughly triangular, flax roughly pentagonal, and hemp is polygonal in cross section. Other fibers, however, such as ramie, cotton, Orlon, Vinyon, and some types of rayon, exhibit rather irregular cross sections of more or less typical character. Wool shows, in general, an approximately circular cross section; the different species of cotton and ramie have widely differing cross sections, most of which give the impression of a collapsed tube, being ribbonlike and having a hollow core (compare Vol. 4, p. 571 and Fig. 2(f)); cellulose acetate rayon usually exhibits a cross section with smoothly rounded lobes, having no cavities or holes and with a very smooth surface, whereas viscose rayons of high tenacity, as used in tire cords, possess an irregularly shaped cross section with a typically crenulated surface. In many cases, the cross sections of fibers are so characteristic of them that they can safely be used as analytical means to distinguish different specimens (see Fig. 2). The uniformity of the cross section in the various individual fibers of a staple sample, and along the length of continuous filaments, is of great importance not only for spinning, knitting, and weaving, but also for the dyeing and finishing of the final fabrics. Denier (or grex) fluctuations can be measured by the electrical conductivity of a thin capillary of mercury through which the fiber is drawn, by measuring the capacity of a condenser, part of which is made up by the yarn under investigation. In certain cases such fluctuations can also be measured by x-ray diffraction.

The *specific gravity* or *density* is usually measured in a pycnometer or in the density-gradient tube and can also be used to determine certain components in a spun yarn or fabric, particularly if only small quantities are present. In such cases, the density-gradient tube can serve to separate the "impurity" (for example, cotton in wool) from the bulk of the yarn or fabric, and a subsequent microscopic and microcoloristic study can definitely establish the identity of the admixed fiber. Table III gives the specific gravities of the most important commercial fibers.

TABLE III. Specific Gravity of Natural and Synthetic Fibers.

Fiber	Sp.gr.	Fiber	Sp.gr.
Steel wire.....	7.5-7.8	Cellulose acetate.....	1.30-1.32
Copper wire.....	8.2-8.4	Protein <sup>b</sup> .....	1.25-1.32
Glass.....	2.5-2.7	Vinyon N.....	1.20-1.22
Quartz.....	2.6-2.8	Orlon.....	1.15-1.20
Saran.....	1.70-1.75	Nylon.....	1.10-1.14
Cellulose <sup>a</sup> .....	1.50-1.54	Polyethylene.....	0.90-0.92

<sup>a</sup> Includes rayon.

<sup>b</sup> Includes silk and wool.

### Mechanical Properties

The mechanical properties of fibers, yarns, cords, and fabrics are in many cases those which determine the commercial value of the material, although sometimes other qualities, such as luster, dyeability, and electrical characteristics, are of preponderant importance. From the point of view of mechanical behavior, the fundamental question is to obtain the deformation of a given sample as a function of the external forces

to which it is submitted and of the time during which these forces act. In general, such tests can be divided into: (1) very short-time dynamic tests, where the time of an individual distortion amounts only to a fraction of a second, after which the sample is permitted to undergo relaxation; (2) normal tests, where the time of the individual deformation is of the order of magnitude of 100 seconds; and (3) long-time tests or creep-and-flow studies, where the experiments extend over many hours and even days.

Considering first the normal tests, it has become customary to specify approximately the duration of a typical experiment and, especially in fiber and yarn testing, to emphasize the stress-strain relationships at constant rate of loading or constant rate of elongation. Extending a given fiber, yarn, or cord under such conditions, one arrives at standard stress-strain curves, in which the

stress in the sample is plotted versus the strain, which it produces. It should be mentioned that it has become customary in fiber testing, where the elongations usually do not exceed 20–25%, to compute the stress in the test specimen by dividing the *initial* cross section into the actual load at any point of the curve instead of using the actual cross section of the strained sample. Figure 3 shows a typical stress-strain curve for a Merino wool fiber indicating that, at first, a considerable stress is necessary to extend the fiber. Later the slope of the curve flattens noticeably, indicating that at higher stresses the fiber extends much more easily until it starts to reinforce again at still higher stresses and, finally, ruptures at about 30% elongation. The initial slope of the stress-strain curve is defined as the *modulus of elasticity* or as *Young's modulus*; it can be obtained by extrapolating an experimental stress-strain curve to very small elongations, or, still better,

by carrying out dynamic measurements, which involve only infinitesimal deformations of the test pieces. The modulus of elasticity is an important quantity in characterizing a fiber, yarn, or cord; it represents its stiffness, by measuring the initial resistance against extension (see Table IV). Table V gives Young's moduli for several commercial fibers as measured by various methods. It shows that the stiffest fibers known are glass, steel, and quartz, followed by Orlon and natural cellulose, such as flax, hemp, or ramie and highly stretched viscose rayon, whereas the most pliant fibers are respun protein fibers, and cellulose acetate rayon. Although the whole course of the stress-strain curve of a fiber or a yarn is indicative of its mechanical properties, it has become customary to use for a preliminary description of a given material only its initial slope and the coordinates of its end point, namely, of the point of rupture. They are called *tensile strength* (tenacity) and *elongation-to-break*, respectively, and depend, to a certain extent, upon the rate of elongation, the temperature, and the presence of swelling agents such as water or plasticizers. "Standard conditions" are usually accepted in the U.S. to be 70°F. and 65% r.h. In 1948, the International Standards Organization adopted conditions of 68°F. and 75% r.h. and recommended them for international use.

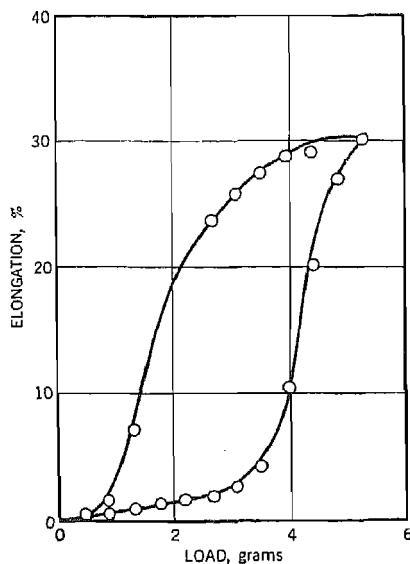


Fig. 3. Stress-strain curve for a Merino wool fiber.



Usually machines measuring stress-strain curves are run with elongations of 12 in. per minute, although it must be noted that different conditions have to be specified if fibers of very different properties have to be investigated. For information on the behavior of textile materials at high moisture contents, the stress-strain curve is measured in the wet state giving the *wet tenacity* and the *wet elongation*. For viscose rayon the wet tenacity is usually inferior to the dry tenacity, whereas the elongation-to-break in the wet state exceeds the dry elongation.

TABLE IV. Relative Initial Stretch Resistance (Stiffness) of Various Fibers (referred to cotton as 1.00).

Fiber	Relative stiffness	Fiber	Relative stiffness
Quartz.....	6-8	Drawn nylon.....	0.6 -0.8
Glass.....	5-7	Orlon.....	0.8 -1.2
Flax and hemp.....	4-5	Silk.....	0.8 -1.0
Ramie.....	3-4	Wool.....	0.1 -0.2
Viscose rayon		Saran.....	0.3 -0.4
Highly stretched.....	1.5-2.2	Vinyon N.....	0.5 -0.7
Moderately stretched.....	0.4-0.6	Acetate rayon.....	0.1 -0.2
Normal.....	0.2-0.3	Respun protein.....	0.05-0.07
Cotton.....	1.00		

TABLE V. Modulus of Elasticity of Some Representative Fibers.

Fiber	Modulus of elasticity, in:		
	Kg./sq.cm. ( $\times 10^{-4}$ )	P.s.i. ( $\times 10^{-2}$ )	Grams/grex
Steel wire	Up to 200	300	—
Quartz fiber	Up to 200	300	—
Glass fiber	150	230	—
Hemp	Up to 150	Up to 200	Up to 100
Orlon	60-70	80-90	50-60
Viscose rayon			
Highly stretched	40-70	55-95	25-45
Moderately stretched	15-25	22-33	12-16
Normal	5-15	7-20	4-10
Cotton	40-60	55-70	25-40
Silk	40-60	55-70	30-45
Wool	35-40	50-60	25-30
Drawn nylon	35-45	45-60	30-40
Respun protein	30-40	40-60	20-30
Vinyon	30-40	40-60	25-30

Also of interest is the resistance of fibers, yarns, and other textile materials toward stress in their strongly bent state. The *loop* or *knot strength* and the *loop* or *knot elongation* are measured by making a loop or a knot in the sample and determining its stress-strain curve up to the point of rupture. Table VI collects a number of data on the various constants just mentioned for the most important commercial fibers; they were all measured at room temperature, with a normal rate of loading and at 65% r.h. for the dry experiments.

Tenacities and elongations-to-break by no means suffice to characterize a textile material, even apart from the long-time tests. Other tests used occasionally are *impact strength*, where the sample is ruptured by a sudden shock usually with the aid of

a dropping pendulum, and various *torsion* and *bending* tests which measure the tendency of a sample to return to its original shape, after having been twisted or bent in a specified manner. In these tests one determines the initial resistance against torsion and bending as well as the final strength of the material under these two types of deformation.

TABLE VI. Various Important Mechanical Properties of Commercial Fibers.

Fiber	Dry tenacity- to-break, g./gret	Dry elongation- to-break, %	Wet tenacity- to-break, g./gret	Wet elongation- to-break, %
Acetate rayon				
Highly stretched	Up to 7.0	3-6	—	—
Moderately stretched	Up to 3.5	10-15	—	—
Normal	1.3-1.8	25-30	1.0-1.5	30-40
Drawn nylon	6.0-8.5	15-20	5.5-7.5	18-25
Hemp, flax, and ramie	6-7	4-6	6.5-7.5	4-6
Vinyon	Up to 4.5	15-30	Up to 4.0	20-35
Viscose rayon				
Highly stretched	3.5-6.5	4-8	2.5-4.5	6-10
Moderately stretched	2.5-4.5	8-12	2.0-3.5	10-14
Normal	1.8-2.5	12-20	1.0-1.8	15-25
Orlon	3.5-5.5	15-20	3.5-5.0	15-25
Cotton	3.0-5.0	4-8	3.5-5.5	4-8
Silk	2.5-5.0	15-20	2.0-4.5	15-30
Wool	1.2-1.7	25-45	0.8-1.4	30-50
Respun protein	0.6-1.0	30-50	0.3-0.5	40-80

The long-time tests, extending over hours and even days, give another class of mechanical properties of fibers and of the textile materials made from them. The simplest of these is the *creep* or *flow* test, which is carried out by measuring the elongation at given conditions, such as load, temperature, and humidity, as a function of time. Since the experiments usually extend from a few seconds to many hours, it is convenient to plot the property measured against the logarithm of time. Creep curves of typical fibers all start with a relatively steep initial slope and flatten out gradually, indicating that a given load produces a certain initial deformation within a relatively short time and that this deformation causes structural changes in the filament which makes it less and less easily extensible. The degree of this "work-hardening" depends upon the prevailing experimental conditions and is characteristic for a given type of fiber. Removing the load after a certain period, and registering the length of the slowly contracting fiber is a way of investigating the *relaxation*, which reflects the manner in which the work-hardened fiber is brought back into equilibrium by the mechanical stresses accumulated in it. In general, it is found that as a result of relaxation, fibers do not return exactly to their original condition, but assume a somewhat extended shape. The area of the hysteresis loop is an indication of the amount of energy which was absorbed by the fiber to cause its mechanical deformation. Figure 4 shows typical creep curves of viscose rayon and nylon, demonstrating that cellulose creeps to a much smaller extent than nylon. It should be noted, however, that wetting out of the relaxed rayon yarn eventually restores its original dimensions almost completely. It is fair to say that the simple (primary) mechanical properties of many fibers, such as the various moduli, tensile strength, elongation-to-break, creep, and relaxation, can be brought at least qualitatively in rational relation to the molecular

structure and supermolecular texture. However, for other more complex mechanical properties, this is not the case. One important property of this kind is the resistance of a fiber to the action of a constant tension over which there is superimposed a periodically varying stress, which may be accompanied by internal friction and by a rise in temperature. Such experiments usually are referred to as *fatigue* or *endurance* tests and one speaks therefore of the resistance of a fiber, yarn, or cord against fatigue. Certain fibers, such as cotton, moderately stretched viscose rayon, Orlon, and nylon, have a very high fatigue resistance, whereas others such as highly stretched viscose rayon or cellulose acetate rayon are distinctly inferior. Resistance against fatigue is the paramount property for yarns and cords to be used in tires and transport belts; it depends in a characteristic way upon certain fine structures of the fibers, but it cannot be claimed that its fundamental aspects are fully understood. Another important endurance property is the resistance of a fibrous material to *abrasion* over long periods

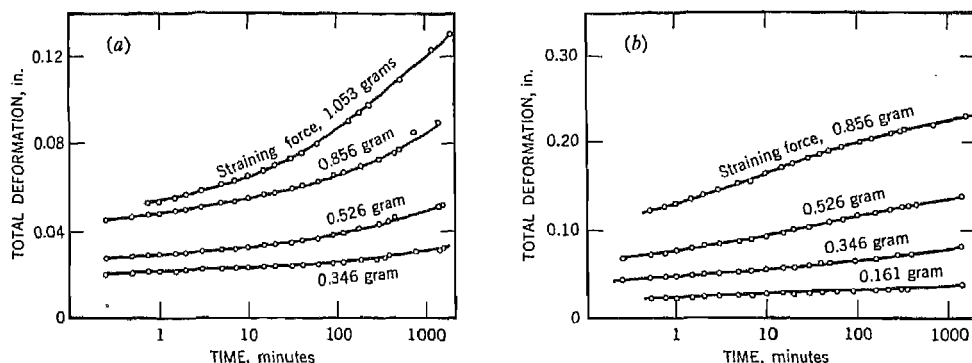


Fig. 4. Creep curves: (a) viscose rayon; (b) nylon (3).

of time and wide ranges of tension, temperature, and humidity; it is particularly important for carpets, furniture fabrics, cordage, and the like and can be at least qualitatively determined by various tests. It has not yet been possible to establish a complete understanding of the relations between structural details and resistance to abrasion.

Other complex mechanical properties of great practical importance are *resilience*, *liveliness*, *softness*, and *hand*; there exist certain devices to estimate them, but as yet there has been little success in relating them with the structural features of the material.

### Thermal, Electrical, and Optical Properties

Heat conductivity, heat capacity, surface roughness, and the capability to enclose air and other gases together are responsible for what is usually called the *warmth* of a textile material. This is an important practical property, which, however, is not yet well understood with regard to its various contributing components. Wool, silk, respun proteins, and Orlon are in this respect superior to all other natural and synthetic fibers, but there are hardly any numerical data available at present. Other important thermal properties of fibrous materials are *sticking point*, *softening* or *melting point*, and *cold brittleness*. The sticking points of cotton, viscose rayon, wool, silk, nylon, and Orlon are well above 200°C., and in general, do not cause much trouble in ironing and

pressing operations. Cellulose acetate and Vinyon, however, have sticking ranges, which, depending on moisture and plasticizer content, may be as low as 150°C., which can lead to serious difficulties through fusing together of individual filaments and yarns. Table VII gives the softening range of some thermoplastic fibers. The melting point of a good fiber-forming polymer should be well above 200°C., preferably even above 250°C. For certain special uses it is important that a fiber should not become brittle at low temperatures (−20°C. and below). Most fibers, with the possible exception of Vinyon and cellulose acetate, remain sufficiently flexible down to temperatures as low as −40 to −50°C.

The most important electrical properties of fibers are *insulating capacity*, *dielectric constant*, and *loss factor at high frequencies* ( $10^7$  cycles per second and more). The insulating capacity is closely related to the water absorption of the material and decreases with increasing moisture content. Nylon and particularly Orlon with their low affinity for water and their high softening ranges are attractive for electrical uses. Dielectric constant and loss factor depend upon the presence of polar groups that can be oriented in an alternating electric field; all fibers mentioned until now contain relatively large proportions of polar groups such as OH, CO, NH, CN, and CCl, and have therefore relatively high loss factors. There exist polymers such as Teflon, Kel-F, Polythene, and Polystyrene, which have very small loss factors ( $1.5 \times 10^{-4}$  and below) and some of them have also been spun into fibers of outstanding electrical performance.

TABLE VII. Softening Range of Some Thermoplastic Fibers.

Fiber	Softening range, °C.	Fiber	Softening range, °C.
Quartz.....	1500–2500	Acetate rayon.....	185–220
Glass.....	500–700	Saran.....	150–180
Nylon.....	230–270	Polyethylene.....	115–125
Orlon.....	220–250	Vinyon N.....	75–90

Optical properties of fibers are, in general, not very important as a quality index for textile uses. It is desirable for fibrous materials to have a considerable *covering power* and for certain uses a more or less pronounced *luster*. Some wool species are rather dull whereas cellulose acetate is a very bright fiber, but the degree of the dullness or brightness depends to a large extent upon the origin and treatment (washing and finishing) of the wool and the preparation and treatment of the cellulose acetate.

### Chemical, Physiological, and Other Properties

Good textile fibers must be resistant to acids and alkalis of moderate concentrations up to about 60–80°C.; they should not be attacked by organic solvents such as hydrocarbons, alcohols, ethers, ketones, and chlorinated paraffins; they should be resistant to the action of light in the presence of oxygen and water and against that of enzymes, molds, and bacteria. They should not irritate the skin and not produce any poisonous or obnoxious products upon heating or combustion. Probably most important of all, they should take up dyes rapidly and uniformly. None of the fibers at present known exhibits all the above qualities to a completely satisfactory degree; each of them represents a different compromise of desirable and not quite satisfactory chemical behavior and it is the character of this compromise which determines the field of the most successful application of each individual material. Cellulosic fibers,

such as hemp, flax, cotton, and viscose rayon, are perfectly resistant to organic solvents, accept and retain dyes satisfactorily, do not irritate the skin, and do not show undesirable behavior on heating and combustion; on the other hand, they are attacked rather easily by acids, do not exhibit great resistance to enzymes and molds, undergo relatively rapid oxidative degradation in the presence of alkalies and oxygen at elevated temperatures, and have a tendency to weaken in prolonged outdoor use. Protein fibers, such as wool, silk, and the various respun animal and vegetable proteins are sufficiently resistant to organic solvents and acids, interact satisfactorily with dyes, do not attack the skin, and do not suffer upon moderate heating; but they are easily attacked by fermentative agents, do not resist the influence of alkalies, shrink considerably upon repeated wetting and drying, and are not too good under severe atmospheric conditions.

Fibers made of cellulose acetate and of copolymers of vinyl chloride with vinyl acetate, and acrylonitrile (Vinyon E and N, respectively) show excellent resistance to acids, enzymes, and molds, and are not objectionable from the point of view of molesting the skin; but they are swelled or even dissolved by many organic solvents, particularly at higher temperatures, are corroded by the action of alkalies, and are weakened or discolored badly upon heating.

Nylon and Orlon fibers are remarkably resistant to all normal organic solvents, sufficiently unattacked by acids, alkalies, and enzymes, and show very good endurance in outdoor use; but they are difficult to dye and eventually show swelling in certain organic solvents at elevated temperatures. Thus, it seems that representatives of the classes of the polyesters, polyamides, polyurethanes, and polyacrylonitriles combine most of the chemical properties (with the exception of dye absorption) that are considered to be important for a good textile fiber, and it appears that appropriate modifications of these materials, obtained by copolymerization, may give fibers of almost completely satisfactory behavior.

An important property of textile fibers is their water absorption in equilibrium with an atmosphere at a given relative humidity and temperature. Some materials like nylon or Orlon have a rather low affinity for water, others such as respun proteins, viscose rayon staple fiber, wool, and cotton a relatively high affinity (see Table VIII).

This enumeration of the physical and chemical properties of the various industrial fibers may serve to give an idea of the empirical facts as known at present; it appears desirable to complement it by a brief discussion of the principles of fiber structure.

TABLE VIII. Water Absorption of Various Fibers at 75°F. and 65% Relative Humidity.

Fiber	Water content, %	Fiber	Water content, %
Respun protein.....	18-25	Cotton.....	7-8
Wool.....	14-18	Acetate rayon	
Viscose rayon		Normal.....	5-8
Normal.....	12-15	Stretched.....	4-6
Stretched.....	10-12	Drawn nylon.....	3.5-4.5
Silk.....	9-11	Orlon.....	3.0-4.0
Hemp, flax, and ramie.....	8-12	Saran.....	<2
Mercerized cotton.....	8-10	Vinyon N.....	<2

### Principles of Fiber Structure

Investigations of the molecular and supermolecular structure of natural and synthetic fibers have shown that, besides the chemical character of each individual fiber,

there exist certain structural principles which are more or less common to all fibers. One of them seems to be that good fiber-forming polymers should be capable of producing areas of a high degree of lateral order, in such a manner that, over a certain length, the molecular chains are arranged in a three-dimensional latticelike pattern.

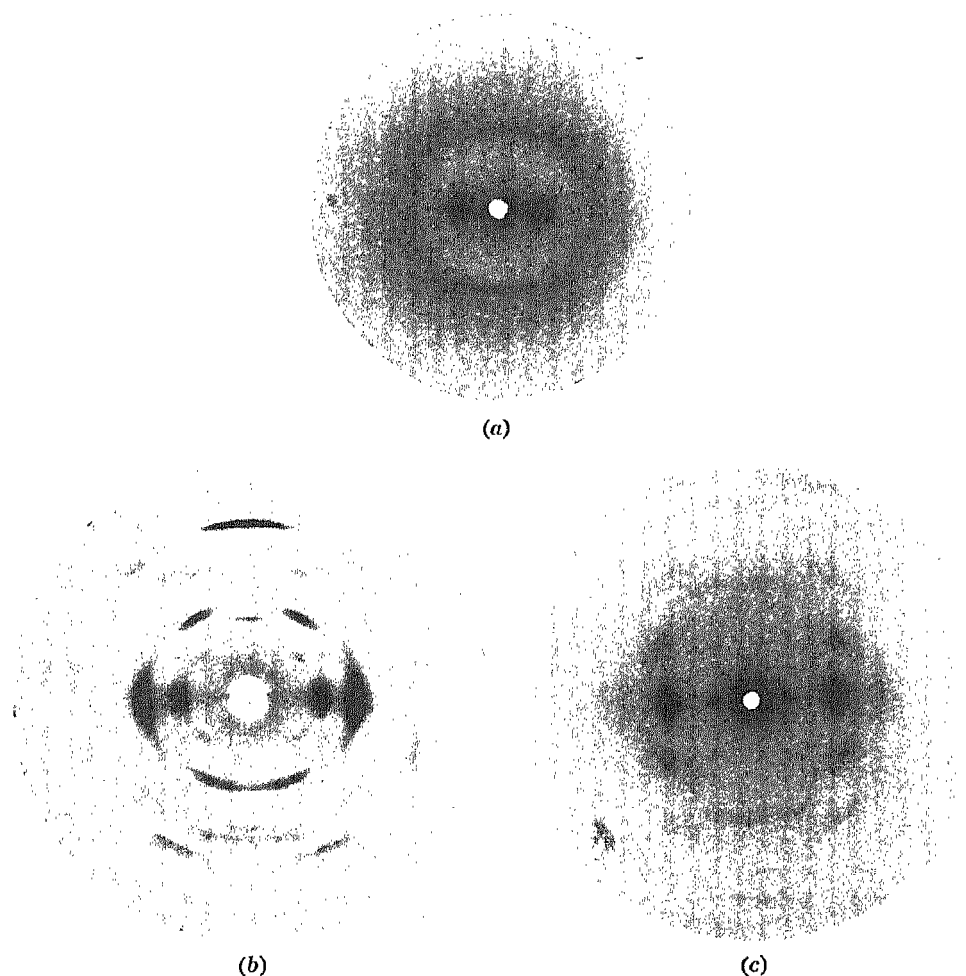


Fig. 5. X-ray diagrams: (a) wool (5); (b) ramie (5); (c) silk (courtesy J. Sikorski, International Wool Secretariat Research Fellow, Textile Physics Laboratory, Leeds, England).

These domains of high lateral order are referred to as *crystallites* or *micelles*. Most fibers consist of a system of crystallites, which are embedded in an amorphous matrix in such a manner that one and the same macromolecule can pass through several crystallites and several amorphous areas in between; in the case of ramie, for instance, it was found that the individual macromolecules have an average extended length of about 10,000–20,000 Å., whereas the average length of the crystallites is of the order of magnitude of 1,500–2,500 Å. It seems to be established that the existence of crystallites or micelles is essential for the exhibition of good fiber properties, but in addition, it must be emphasized that the degree of crystallinity varies considerably from fiber to

fiber. Experience has shown that the degree of crystallinity is related to the modulus of elasticity, the stiffness, the tenacity, and particularly to the dye absorption of the fiber, and that any change of it affects these properties to a noticeable degree.

Wool, Vinyon, and normal cellulose acetate show x-ray diagrams which indicate the presence of only a very small proportion of laterally well-ordered domains. On

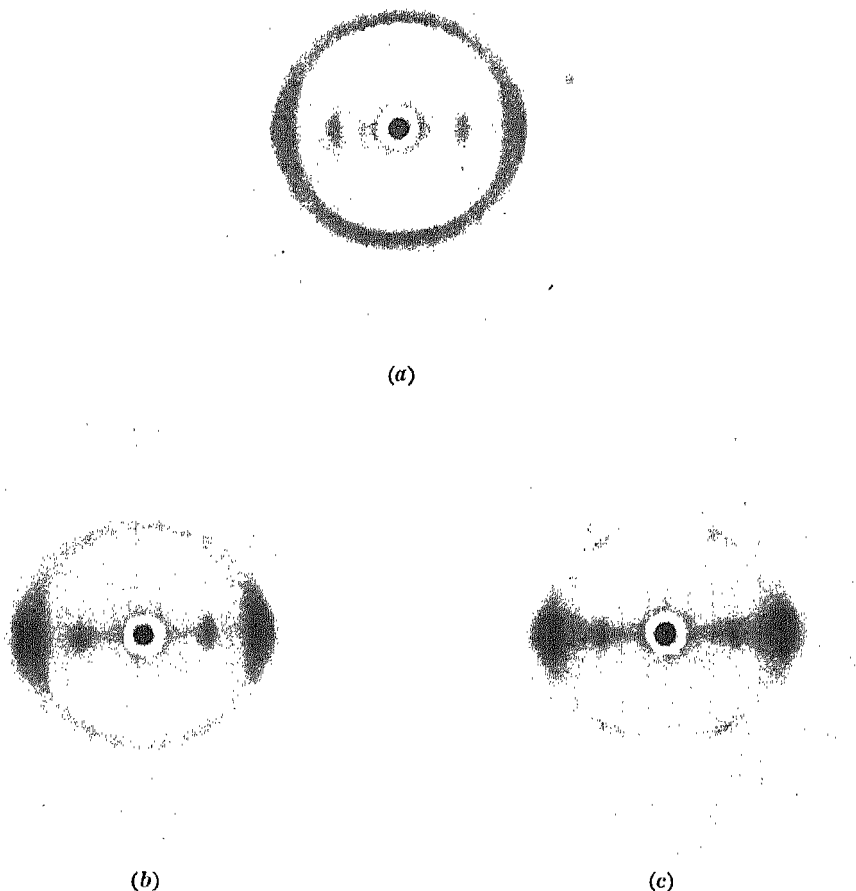


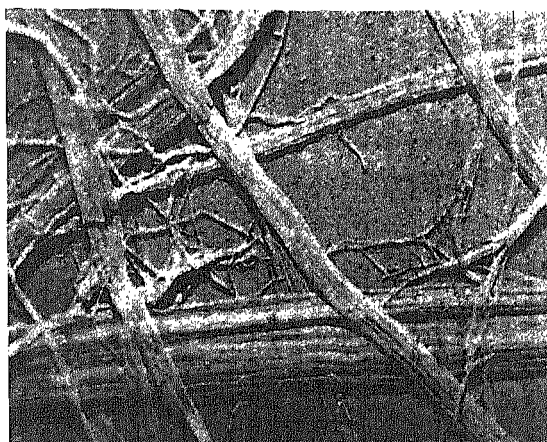
Fig. 6. X-ray diagrams of unstretched and stretched rayon: (a) unstretched; (b) moderately stretched; (c) highly stretched.

the other hand, silk, ramie, flax, hemp, cotton, highly oriented viscose rayon filaments, and drawn nylon exhibit x-ray patterns which indicate the presence of a high percentage (probably 70–80%) of crystallites. (See Fig. 5.)

Another important factor is *orientation*. It was found that all natural fibers exhibit a certain orientation of the crystallized areas, depending upon the type, origin, and treatment of the fiber. Artificial fibers can be produced in such a way that there is virtually no orientation, if the spinning is carried out under essentially relaxed conditions; on the other hand, it is observed that stretching during spinning always leads

to a more or less pronounced orientation of the existing crystallites, which expresses itself in the x-ray diagrams by the appearance of sharp and symmetrically arranged diffraction spots as clearly visible in Figure 6. Orientation of the crystallites or micelles probably also results in a certain orientation of the disordered or amorphous areas, although this orientation is more difficult to establish from the x-ray diagrams and from other data. It has been found that increased orientation leads to increased modulus of elasticity, tensile strength, and optical anisotropy, but to a diminution of the elongation-to-break, the resistance to abrasion, and the absorption of dye.

A third important aspect of fiber structure is the existence of *fibrils*. It has long been known that many natural fibers consist of microscopic or submicroscopic elongated elements, which can be separated from each other relatively easily, whereas the interior of each fibril is much more closely packed. The electron microscope has made



Courtesy American Viscose Corporation.

Fig. 7. Fibrils in secondary wall of cotton.

it possible to study the fibrils in many natural and synthetic fibers and to establish their exact dimensions. Figure 7 shows as an example the fibrils in the secondary cell wall of cotton and demonstrates that they are strands of an average diameter of 300–500 Å. and of virtually infinite length. They are arranged, in this case, parallel to each other and at a certain angle to the axis of the fiber. The fibrils in native samples are evidently the result of certain phenomena occurring during the growth process of the fiber and represent the natural morphology of the system. However, it was found that artificial fibers, such as viscose rayon, acetate rayon and nylon, also can be disintegrated into fibrils, which in general are less homogeneous and thicker than those of native fibers. It is not yet clear how the existence of fibrils in synthetic fibers should be explained and how their dimensions and arrangement depend upon the method of formation of the filament. In wet-spun fibers, such as viscose rayon, it appears that the fibrils are a consequence of a quasiperiodic character of the precipitation process and are related to the phenomenon of skin formation; sometimes they are easy to separate from each other and clearly recognizable, sometimes their existence is only weakly indicated. The relation of the fibrillar structure of a fiber to its mechanical properties is not yet clearly understood, but it seems that the existence of fibrils of



considerably different thickness and orientation may lead to stress accumulation and hence to premature rupture. It also seems that the homogeneity of the fibrillar structure of a fiber is important for the resistance of the fiber against fatigue and abrasion, but there exist as yet no quantitative formulas to express these relationships.

### Tests to Determine the Chemical Nature of Fibers

The complete chemical analysis of an organic fibrous material can be a rather difficult and delicate task, particularly if the sample consists of a mixture of different species and if only a small quantity is available for the investigation. The following general procedure can be recommended to get an idea of the chemical nature of a given fibrous material or of the composition of a fabric containing several different fibers.

(1) The sample is treated with acetone in a Soxhlet extractor for several hours. If it dissolves completely, it consisted either of cellulose acetate or of Vinyon E. The distinction is made by precipitating the polymer from its dilute (1–2%) solution in acetone with methanol and analyzing the resulting dried white powdery material for acetyl or chlorine, respectively. Cellulose triacetate fibers would not respond to this procedure because they are not soluble in acetone. However, there is no commercial production of fibers of this polymer at this time and it is, therefore, unlikely that any industrial fabric will contain this material. If only part of the sample dissolves, the remaining fabric is weighed and the amount of cellulose acetate and/or Vinyon E is determined by difference. The polymer in the extract is again precipitated and analyzed for acetyl and chlorine contents. Commercial cellulose acetate contains about 54.5% acetate, Vinyon E contains 90–95% chloride and 5–10% acetate. After this procedure, which determines and removes cellulose acetate and Vinyon E, the sample is extracted for 3 hours with *N,N*-dimethylformamide. Orlon and Vinyon N are extracted and can be precipitated from a dilute (1–2%) solution in *N,N*-dimethylformamide with heptane. Quantitative nitrogen and chlorine determinations provide a distinction between these two fibers: Orlon contains about 25% nitrogen and no chlorine, Vinyon contains a few per cent nitrogen and about 50% chlorine. Orlon and Vinyon N yarns, if highly drawn and strongly twisted, dissolve only slowly in dimethylformamide; it is therefore advisable to shred the fabric before treatment to a fluffy powdery mass which offers a larger surface area to the applied solvents. It must be mentioned here that certain nylons, specifically type “6” nylon (Perlon L) and type “6–10” nylon, are also to a certain extent soluble in dimethylformamide. But these materials are, at present at least, not used in textile goods, but only as relatively thick monofilaments in sutures, strings, and bristles.

(2) The residue after extraction with acetone and dimethylformamide consists of cellulose, proteins, and nylon. A quantitative separation of these three fiber-forming polymers is rather difficult and no general procedure can be given for it. A qualitative insight into a mixture of these fibers in a fabric can be obtained by pulling out individual filaments and inspecting them. If they are longer than 10 in., wool and cotton are excluded and the filaments must be either silk, flax (hemp, ramie), viscose rayon, or nylon. Short fibers can be any of the above types, because most continuous filaments, such as viscose rayon or nylon, are frequently used as staple fibers. Microscopic inspection of the fabric itself and of the cross sections of the removed individual filaments will, in most cases, give enough data to establish the presence or absence of the various constituents. If the fabric is undyed or only slightly dyed the microscopic observations can be supplemented with spot tests for cellulose and proteins, which further

assists in distinguishing between native and regenerated (mercerized) cellulose and between silk and wool, respectively. If a fabric is deeply dyed and tightly woven, it can occur that the individual filaments do not exhibit characteristic cross sections or staining properties any more and that microscopy does not reveal much about the sample. In such cases x-ray diffraction patterns have proved to be very helpful in establishing the presence or absence of certain constituents in a fabric. They even permit distinguishing between rayons of different degrees of orientation such as "textile" type and "tire-cord" type or between cotton and flax (hemp, ramie) and between silk and wool.

A semiquantitative separation of nylon, protein, and cellulose constituents in textile goods can be carried out by analyzing the finely shredded fiber mass in a density-gradient tube covering the range from 1.10 to 1.60. Nylon-type fibers accumulate between 1.15 and 1.20; proteins cover the range between 1.38 and 1.42, whereas cellulose fibers are all above 1.45. Normally dyed fibers do not greatly deviate from these values but for heavily pigmented specimens the density method is not entirely reliable. To determine quantitatively the percentage of any one of the three types of fibers in a mixed fabric, it is necessary to use special procedures in any given case. If the amount of cotton or rayon is to be found in a blend with wool, silk, or nylon, it is possible, for instance, to treat the sample with concentrated hydrochloric acid at room temperature thereby degrading the cellulose to glucose, which can be determined as such. A similar procedure can be employed to determine quantitatively the amount of nylon in a blend with wool or silk. Hydrolysis with hydrochloric acid at elevated temperatures degrades the nylon to its constituents, which can be determined analytically.

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H. F. MARK

### FIBERS, VEGETABLE

Vegetable fibers of plant origin are used in a variety of industrial products. Cotton and flax, only two of the many fibers used, are best known because of their extensive use in personal living (see *Cotton*; *Linen*). However, of the estimated 20 billion lb. of vegetable fibers produced annually on a commercial scale, it is estimated that fully  $\frac{1}{3}$  are fibers other than cotton.

For general industrial differentiation, vegetable fibers are classified as "hard" or "soft" according to the relative degree of fiber fineness and associated stiffness in the raw state. The hard fibers, including abaca, agaves (cantala, henequen, and sisal), istle, mauritius, phormium, and a number of others of lesser importance are obtained from the leaves of plants growing mainly in the Tropics. These are used most ex-

tensively for cordage. The hard fibers also include coir, the brown, coarse, bristlelike fiber enveloping the common coconut. The soft fibers include flax, hemp, jute, ramie, and a number of similar fibers of lesser importance. Ordinarily these are the fibers obtained from stems of reedlike plants, and are called bast fibers. Soft fibers also include seed hairs such as cotton or the seed-pod fiber kapok.

The bast fibers, running the length of the stem and located in the inner bark, are surrounded by thin-wall enveloping tissue and cemented together by pectic gums. The general practice of separating these fibers from the woody stalk is to employ a retting process, whereby the fiber stems are partially disintegrated by bacteriological action and separation from the stalk is facilitated. The hard fibers are ordinarily located near the surfaces of the plant leaves and are separated by mechanical scraping processes which remove them from the pulpy adhering leaf tissue.

It is estimated that more than 1000 species of plants in the Western Hemisphere alone are used for fibers. Most of these, however, are locally used. The fibers described subsequently are those generally produced in sufficient quantities to be considered of commercial importance. When such fibers are produced, they are classified into a number of grades based mainly on the physical characteristics which are influenced by environmental conditions. Because of the magnitude of variation between grades of any particular fiber, it can be appreciated that physical and chemical data ascribed to the respective fibers are accurate only to the extent of direct association with the fiber the test sample represented. Test data in the following, unless associated with a definite grade, are to be considered indicative of general attributes.

TABLE I. Tensile Strength and Wet Strength Loss of Common Cordage Fibers.

Fiber	Tensile strength dry, ft. <sup>a</sup>	Wet strength loss, %	Fiber	Tensile strength dry, ft. <sup>a</sup>	Wet strength loss, %
Abaca.....	153,000	21.0	Istle.....	74,000	—
Hemp.....	86,000	42.2	Jute.....	84,000	12.5
Henequen.....	86,000	14.3	Sisal.....	120,000	12.5

<sup>a</sup> Tensile strength is reported on the basis of breaking length—the product of the breaking strength and the number of feet to the pound of yarn tested. Since feet per pound for a constant density is a direct measure of cross-sectional area, breaking length measures strength per unit area.

TABLE II. Fiber Imports into the U.S., 1949.

Fiber	Imports, long tons	Value, \$	Fiber	Imports, long tons	Value, \$
Abaca.....	43,093	22,393,485	Jute.....	60,999	23,516,068
Cantala...	396	107,057	Kapok.....	1,889	1,239,722
Coir.....	3,677	753,731	Phormium.....	5	938
Flax.....	1,084	1,075,466	Ramie.....	62	18,182
Hemp.....	75	74,570	Sisal and henequen...	126,271	36,516,703
Istle.....	6,360	1,215,918	Sunn.....	452	87,105

Table I (6) gives the tensile strength and loss in tensile strength when wet of a few common cordage fibers, which were tested after being made into very fine yarns. The A.S.T.M. has issued a standard for identifying fibers in textiles (A.S.T.M. D276-49). Table II gives fiber imports into the U.S. for 1949.

## Hard Fibers

### LEAF FIBERS

**Abaca** is the fiber extracted from the plant *Musa textilis*, native to the Philippine Islands. Commonly known as Manila fiber or Manila hemp, abaca is the strongest of all vegetable fibers and the most important fiber used for the manufacture of heavy rope and cordage for marine, industrial, and farm uses.

The abaca plant is practically indistinguishable in appearance from the banana plant *Musa sapientum*, differing only slightly in the color, shape, and size of the leaf. However, the fiber from a banana plant is very weak in comparison with that from abaca. When mature, the individual abaca plant consists of 12-30 stalks radiating from a central root system. Each of these stalks is usually from 8 to 20 ft. tall with a trunk 4-9 in. at the base. Resembling somewhat a huge bunch of celery, the cylindrical stalk is bare of foliage except toward the top, where it opens out into a large leaf structure. The cylindrical trunk of the stalk is formed by a number of crescent-shaped sheaths overlapping each other on the stem in concentric layers, which are pressed against each other tightly thus forming the compact stalk trunk. Near the top of the stalk, the sheaths expand into the overhanging leaf structure. The sheaths before expanding range in length from 6 to 12 ft., are 5-8 in. wide, and about  $\frac{3}{8}$  in. thick at the center. The fibers run lengthwise in the sheaths. In each sheath there are three distinct layers, the outermost surface layer containing the fibers. The sheaths, in addition to varying in length and width, also vary in color. In order to obtain the fiber, the mature stalks are cut off at the roots and at a point just below where they begin to expand into the leaf structure. In the Philippines, the stripping method is generally used. This consists of separating the fiber layer from the cut sheath by inserting a knife just under the layer and pulling a fiber strip or "tuxy," 2-3 in. wide, off the sheath. When a sufficient number of strips have been collected, they are bundled and carried to a central shed for the cleaning operation. This consists of pulling the fiber strip under a knife, which is pressed against the strip. This cleaning operation requires strenuous labor in pulling by hand. Modern plantations notably in the Davao region of the Philippines have replaced this hand-pulling operation with power-driven pulling machines to accelerate production. After stripping, the fiber is air-dried, care being exercised to keep the fiber out of the rain and direct sun to avoid hurting the fiber with respect to color and luster. The clean dry fiber yield amounts to 2-3% of the weight of the stalk.

In addition to the foregoing stripping method, a small proportion of Philippine abaca fiber (less than 5%) is produced by mechanical decortication. In this process, described more fully under sisal fiber (see p. 470), the sheaths are fed into a decortivating machine in which the pulpy material is scraped from the fiber mechanically, washed, and dried. The abaca fiber so produced is not considered quite as good as the hand-cleaned variety, having less sheen and being harsher in texture. Abaca fiber grown in Sumatra and Central American countries is exclusively machine-decorticated. The fiber yield by this method averages about  $3\frac{1}{2}\%$ .

The Philippines constitute the main source of abaca, contributing before World War II in excess of 95% of the total supply. Since 1945, this proportion has dropped to about 80%. By virtue of its importance, Philippine abaca is carefully graded under direction of the Philippine Government. For grading purposes, the long cordage fiber is classified into four groups determined by the fineness of the fiber and degree of separation of the individual fibers. Each group is further subdivided according to the range of color and associated fiber length. Currently there are 18 grades, designated AB, CD, E, F, S2, S3, I, J1, G, H, J2, K, L1, L2, M1, M2, DL, and DM. These grades range in color from practically white to dark brown. The abaca fiber grown in the Davao Province in the southern part of the Island of Mindanao is considered premium fiber. It is longer and stronger than the corresponding government grades produced elsewhere, and is generally lighter in color but bolder in texture.

Central American abaca, which now accounts for 15% of the world abaca supply, is produced in Panama, Costa Rica, Guatemala, and Honduras, and is currently avail-

able in two grades: clear and streaky. Sumatra abaca is available in four grades: superior, good, fair, and fair X.

Abaca is a multicellular fiber made up of fibrovascular bundles. Individual fibers of commerce attain a length of 12 ft. or more and a diameter range of 0.2–1 mm. The ultimate cells are 3–12 mm. long and 16–32  $\mu$  in diameter. The chemical analysis of a grade J2 Philippine abaca has been given as follows: ash, 1.02%; water, 11.83%; aqueous extract, 0.97%; fat, wax, and gum, 0.63%; pectic matter, 21.83%; cellulose, 63.72%.

Abaca fiber is used chiefly for ropes, cordage, and twines requiring highest strength, durability, and reliability. An additional important use is in the manufacture of strong Manila paper or a fine strong tissue paper.

**Mauritius** is the fiber obtained from the plant *Furcraea foetida*, or the *Furcraea gigantea*, native to Brazil, where it is known as *piteira*. Because it is cultivated on a large commercial scale only on the Island of Mauritius and only to a limited degree in Brazil, Natal, and India, the fiber is termed Mauritius hemp more frequently than *piteira*. In Mauritius, the fiber and plant are known as *aloe*. In appearance and characteristics, the plant resembles the agaves, except that the leaves are heavier and larger. The fiber is extracted from the leaves by a simple mechanical decorticating process, in which the crushed leaves are scraped free of the pulpy material, washed, steeped in a soapy solution, and then sun-dried. The dry fiber yield is 1½–2½% of the green-leaf weight.

Mauritius fiber is 4–7 ft. long, white in color, and much finer and softer than the other hard fibers, but extremely weak. The cells are uniformly broad and cylindrical. Chemically, the fiber is lignified and similar in composition to sisal. Five grades have been standardized based on cleaning and color: extra prime, prime, very good, good, and fair. Because of its low strength the fiber is generally used for cordage, blending it with darker fibers to improve color.

**Phormium** is the fiber extracted from the plant *Phormium tenax*, native to New Zealand. Although it is commonly called New Zealand flax or New Zealand hemp, neither fiber nor plant has bast characteristics. The plant is a perennial consisting of a fan-shaped cluster of leaves 5–13 ft. long and 2¼–4 in. wide. It is green in color with a red midrib and red margins. The fiber is decorticated from the cut leaves by a mechanical decorticating process, similarly to sisal, and then washed and sun-dried. The yield of fiber is 10–15% of the weight of the green leaves.

Phormium is light tan to nearly white in color, resembling abaca more than any other fiber. The fiber length is 5–8 ft. or longer and it is considerably softer and finer than the other hard fibers. The ultimate cells are regular, round in cross section, and ranging from 0.19 to 0.59 in. in length and from 10 to 20  $\mu$  in diameter. Chemical analysis of phormium shows: ash, 0.63%; water, 11.61%; gum (water-soluble), 21.99%; fat, 1.08%; pectin bodies, 1.69%; cellulose, 63.00%.

Like other hard fibers, phormium is graded according to color, length, strength, and cleanliness, and subgraded into eight designations: superior, fine, good, fair, fair high-point, fair low-point, common, and rejected. The fiber is used principally for cordage and twine, generally mixed with abaca or sisal. In New Zealand, the better-quality fiber is spun into fine yarns that are used for fabric weaving.

**Sisal** is the fiber extracted from the three varieties of agave plants cultivated extensively in Indonesia, the Philippines, British and Portuguese East and West Africa, Cuba, Mexico, Brazil, and Haiti. Since the term sisal encompasses fibers that

have different physical characteristics, it is generally qualified by the country or district of origin. Where used without such qualification, sisal most frequently signifies the fiber from *Agave sisalana*, sometimes called true sisal or sisalana. All agaves are native to America. Cultivation elsewhere has been accomplished by transplanting from the Western Hemisphere.

The agaves are characterized by rosettes of fleshy leaves, usually long and narrow, which grow out from a central bud. In the early stages of growth, the leaves are erect, but as they mature they gradually spread out until they stretch out horizontally. At this stage, the leaves are from 3 to 6 ft. long, 4–6 in. wide, and about  $\frac{1}{4}$  in. thick at the center. The fibers lie embedded longitudinally in the leaves, being most abundant near the leaf surfaces. The leaves contain about 90% moisture, but the fleshy pulp is very firm and the leaves are rigid. The fiber must be removed from the leaves as soon as they are cut, for if they become dry the fibers adhere to the pulp and are apt to be damaged in the cleaning. Fiber removal is accomplished by scraping away the pulpy material, generally by a mechanical decortication process.

In the decortication process, the leaves are fed at a rate of 200–300 per minute through sets of fluted rollers, which crush them. The crushed leaves are then held firmly at their centers and both ends of the leaf are passed between pairs of metal drums several feet in diameter on which are mounted scraping blades. As the leaf ends pass between the rotating drums, the pulp is scraped away. The center of the leaf, still containing pulp where it was held, is now released and offset so as to permit a further scraping action at this point. The fiber strands are then washed and either air-dried or artificially dried. In Java and East Africa, when choice grades are required, the dried fiber is brushed by being held against a revolving metal drum to remove remnants of dry adhering pulp.

The three varieties of sisal available commercially are: *Agave sisalana*—commonly known as African sisal, Java sisal, Haitian sisal, or Bahama sisal; *Agave fourcroydes*—commonly known as henequen, Mexican sisal, or Cuban sisal; and *Agave cantala*—commonly known as cantala, Manila maguey, or Cebu maguey. All varieties are used in the manufacture of hard fiber cordage.

*Agave sisalana*. This variety of sisal fiber, particularly the Java sisal, is regarded as the choicest of all the sisal fibers from the viewpoint of strength, color, and cleaning. Ranging in color from almost white to a light strawy cream color, the fiber is regarded as the best substitute for abaca in Manila rope. The commercial fiber ranges in length from 24 to 64 in. and from  $\frac{1}{8}$  to  $\frac{1}{2}$  mm. in diameter. It is generally a little more flexible than henequen, the ultimate cells composing the fibers also being slightly finer. The cells are polygonal in outline, with average major diameter  $15.8\ \mu$  and the minor diameter  $10.8\ \mu$ . A typical analysis of this sisal fiber shows: moisture, 6.2%; ash, 1.0%; alcohol-benzol soluble, 1.1%; lignin, 14.5%; cellulose, 77.2%.

This sisal fiber is graded according to the country and district of growth, and further subgraded according to color, cleaning, and length. There are six Java grades designated A, B, C, X, Y, and Z; seven East African grades designated 1, 2, 3 long, 3 short, A, B, and rejects; and six Haitian grades designated A or 1, B or 2, X, Y, C, and S.

*Agave fourcroydes*. Production of this variety of sisal fiber, generally called henequen, constitutes a main industry in the state of Yucatan in Mexico. Ranging in color from almost white to reddish yellow, this sisal fiber is considered inferior to the *Agave sisalana* fiber with respect to strength, cleaning, texture, and length. Henequen fiber ranges in length from 24 to 60 in. and from  $\frac{1}{8}$  to  $\frac{1}{2}$  mm. in diameter. Each fiber of commerce consists of one or usually more fibrovascular bundles composed of elongated thick-walled cells 1.5–4 mm. long. The average major cell diameter is  $22.2\ \mu$  and the minor  $11.6\ \mu$ . The individual cells are larger than sisal, with rounded angles

and much less uniformity. A typical analysis of a henequen fiber shows: moisture, 4.6%; ash, 1.1%; alcohol-benzol soluble, 3.6%; lignin, 13.1%; cellulose, 77.6%.

Mexican henequen fiber is graded into seven grades according to the color, cleaning, and length; the grades are designated AA, A, B, B1, M, C, and M1. Cuban henequen is used primarily for the manufacture of cordage in Cuba and is generally comparable to Mexican henequen. Three grades A, B, and C are exported; they are comparable to the corresponding Mexican grades.

*Agave cantala*. This variety of fiber, yellowish to brownish white in color, is produced commercially in the Philippines and Indonesia, and is somewhat lighter in color, softer, and finer than sisal or henequen, but weaker. The fiber is prepared in the Philippines by retting the leaves in sea water, then cleaning by hand or by a mechanical decorticating method like the other sisal fibers. Retted fiber lacks luster, is rough, harsh, and dusty. It is regarded as inferior to the machine-decorticated fiber, and because of its salt content, which attracts crickets, cannot be used for binder twine. In Indonesia, the fiber is prepared without prior retting, by the mechanical decortication method used for sisal fiber. The cantala fiber so prepared is comparable in strength to sisal. The fibers are somewhat round in cross section. The individual cells are closely packed and mostly polygonal in outline with average major diameter 16.4  $\mu$  and minor diameter 13.8  $\mu$ . A typical analysis of this fiber shows: moisture, 5.5%; ash, 1.4%; alcohol-benzol soluble, 3.2%; lignin, 14.1%; cellulose, 75.8%.

Manila maguay fiber is graded according to the manner of decortication, that is, retted or machine-decorticated, and subgraded into three grades, designated 1, 2, and 3. In quality it ranks lowest of all the fibers in commercial use. Java cantala, on the other hand, because of its softness, fineness, and strength, commands a premium over sisal in the commercial market.

*Istle* is a general term for a short, coarse, hard fiber obtained from the leaves of agaves or related plants growing wild in northern and central Mexico. The three varieties commercially produced are known as tula istle (*Agave lecheguilla*), jaumave istle (*Agave jaumave*), and palma istle (*Samuela carnerosama*). In commerce, it is customary to use the term tampico fiber for all three varieties of istle indicated. The agave istles resemble small agave sisal plants with leaves 12–40 in. long and 1–2 in. wide. The palma istle plant resembles a small palm tree, with leaves, which yield the fiber, radiating from the top of the plant. The fiber is obtained by a hand-scraping process and subsequent sun drying. The palma istle leaves, however, are so gummy that they must be steamed before scraping. The fiber yield is about 15% of the weight of the green leaves.

Tula istle is nearly white in color. The fiber ranges from 8 to 20 in. in length, and is the coarsest and stiffest agave fiber of commerce. It is used mainly in the brush and upholstery industries.

Jaumave istle is finer in texture than tula istle and nearly as strong and flexible as sisal. The fibers range from 12 to 30 in. in length, and in a brush most closely resemble an animal-fiber brush, hence constituting the most valuable istle brush fibers.

Palma istle is finer in texture than tula istle. The fibers range from 12 to 30 in. in length, but are regarded of lower quality than tula or jaumave istles because of their yellowish color and somewhat brittle nature. This fiber is used in the manufacture of coarse twines and poorer-quality brushes.

A chemical analysis of tula istle shows: moisture, 5.60%; ash, 1.65%; alcohol-benzol soluble, 1.90%; lignin and related substances, 17.37%; cellulose, 73.48%.

## MISCELLANEOUS HARD FIBERS

**Coir** is the fiber enveloping the common coconut, the fruit of the coconut palm tree *Cocos nucifera*. Before the availability of abaca in the early 19th century, coir was of great interest to European ropemakers, because the coir rope with its lightness, high-stretch characteristics, and resistance to salt water surpassed the hemp ropes then used extensively for marine work.

The fiber is extracted from the split husks from which the coconut has been removed for the copra trade. The husks are immersed in brackish shallow sea water for a period of 1-8 months. This retting process dissolves the gum by which the fibers are bound. Hydrogen sulfide is produced during this retting process. When the husks are thoroughly softened, they are removed from the water and the fiber is beaten out on stones with a wooden mallet, and then dried in the sun. In addition to this hand-beating process, mechanical decorticators are also used on a limited scale. The nuts yield about 5% of their weight in dry fiber. The chief centers of the industry are the Island of Ceylon and a section of the Malabar Coast in southwest India. A small amount has in the past been produced commercially in the Philippines.

Coir fiber is brown in color, harsh, and rarely exceeds 10 in. in length. A considerable quantity is used for the upholstery trade. For cordage or fabricating use, coir is supplied as a two-ply cord about  $\frac{3}{16}$  in. in diameter or less and twisted by hand where the fiber is produced. This cord is supplied in grades designated by the district of production. Aratory and Anjengo are two of the commercial grade designations, each further subgraded into A, AA, AAA, 1, 2, etc., depending upon the uniformity and fineness. The chief use of the cord in the U.S. is for weaving matting or other floor coverings. The fiber is also used for brushes.

**Esparto** is a dried wild grass *Stipa tenacissima* or the allied grass *Macrochloa arcuaria* known as alfa, supplied in commercial quantities from Algiers and Tunis. Resembling coarse brittle broomstraw, 1-1½ ft. long and ½-2 mm. in diameter, the material has a high cellulose content, and for this reason is used in the manufacture of certain types of paper. Only a relatively small tonnage is used in the U.S. Purchase is generally on the basis of a sample.

## Soft Fibers

## BAST FIBERS

**Hemp** is the fiber extracted from the annual plant *Cannabis sativa*. Originating probably in Central Asia, it will grow readily in temperate and subtropical climates. The hemp plant is grown either for fiber from the stem, oil from the seeds, or drugs from the flowers or leaves. Marijuana (see *Hypnotics and sedatives*) is the narcotic derived from the related hemp plant *C. indica*, which is not a commercial fiber-producing hemp plant. However, the Marijuana Tax Act of 1937 encompasses the hemp-fiber plant *C. sativa*. The culture of hemp and the transfer of hemp in various forms, including the seed, is subject to so-called licensing regulation of the Bureau of Internal Revenue. Hemp fiber is produced commercially in the greatest amounts in the U.S.S.R. and Italy. The fiber is produced in smaller amounts in the U.S., Chile, and several European countries.

When mature, the stalks range in height from 4 to 15 ft. and are about as thick as a man's finger. They are generally smooth and without branches or foliage except at the top. The stem structure is hollow. Thin-walled tissue adjoins the hollow, and outside this is a layer of woody substance. The next layer consists of gummy tissue which cements the fiber layer to the woody layer. The fiber or bast layer is enveloped by a thin bark which constitutes the outside of the stalk.



In the U.S. and U.S.S.R. the stalks are dew-retted to separate the fiber. Italian hemp is water-retted. Dew-retted hemp is generally grayish or brownish in color. Water-retted hemp is usually light tan in color, softer, and finer in texture. In dew retting, the stalks are spread out thinly and evenly over the field. Fermentation induced by the heat, dew, and rain decomposes the gummy tissue. The stalks are then dried and ultimately taken to the scutching mill for the scutching operations, during which the fiber is removed from the stalk.

Hemp stalks grown in Italy are water-retted. Bundles of stalks are immersed in water in special construction retting pits or canals and kept immersed until fermentation has been completed, generally a period of 7–10 days. The stalks are removed and dried by setting in shocks before being scutched.

In the first scutching operation, the woody portion of the stalk is broken up into small lengths by beating the stalk with a hand-operated brake or, in a modern operation, by passing the stalk through a number of pairs of heavy fluted rollers. The small pieces of the woody portion called hurds still adhering to the fibers are removed in subsequent beating or coarse-brushing operations. A third operation, called hackling, by which the fiber is drawn over a set of coarse, sharp-pointed steel pins to remove extraneous materials and short fibers, may also be used. Short fibers are termed *tow*; the long fibers, extending a substantial portion of the length of the stalk, are termed *line*.

The characteristics determining the grade of the line fiber are the region of growth, color, fine-spinning qualities, length, and cleaning. Italian hemsps are classified as either Bologna or Naples grades; the Bologna fibers being subgraded further into 9 grades. The Naples hemp is subgraded into 4 grades. Russian hemp is classified into two general groups—*siretz* or uncleaned hemp, and scutched or cleaned hemp. Siretz designations HO, O, I, II, III are subgraded into six groups according to the districts and counties where produced. Scutched or cleaned-hemp grade designations HOF, HOM, OF, OM, M, No. 1, I, II, and *uchet* are subgraded into four groups according to the quality of the fiber and care in cleaning.

U.S. hemp is graded according to the state in which it was grown and further subgraded according to length and strength. American-grown hemp ranges in color from slate gray with a definite sheen to a dull greenish-brown strawlike color.

Hemp fibers are flat ribbons ranging from 40 to 200 in. in length and  $\frac{1}{2}$ –5 mm. in width. The ultimate cells are blunt-pointed, but some have forked ends; they are 5–55 mm. long and 16–50  $\mu$  in diameter. A chemical analysis shows: hygroscopic water, 8.88%; ash, 0.82%; aqueous extract, 3.48%; fat and wax, 0.56%; intercellular matter and pectin bodies, 9.31%; cellulose, 77.77%.

In Europe hemp is used for fabrics in competition with flax. In the U.S. hemp is used chiefly for strong twines, or for marine specialties such as tarred cordage, oakum, and packings.

**Jute** is a fiber produced from the stem of either of two species of the herbaceous annual plant *Corchorus*, which are so nearly alike that they are not readily distinguishable except by the seed pods and seeds. *C. capsularis* is the round-pod jute and *C. olitorius* is the long-pod jute. Both species are cultivated in a number of countries. However, Pakistan and India are the main sources of production. The round-pod jute or white jute, as it is usually termed in the trade, is very light in color. The long-pod jute is known in the trade as *tossa* or *daisse*.

Practically all jute fiber is produced in Bengal and adjacent provinces, where a warm climate and heavy rainfall prevail during the growing period. While jute of both species is produced in these areas, the round-pod jute is grown more extensively. Both species have cylindrical stalks 6–12 ft. tall and  $\frac{3}{8}$ – $\frac{1}{2}$  in. in diameter and are light green in color. When the stalks are in the early pod stage they are considered sufficiently mature to be cut (or if pulled, the roots are cut off) and tied in bundles, and water-retted similarly to hemp. After retting for 10–20 days, the bark together with the fiber is separated from the woody portion of the stem by beating with a flat wooden mallet, whipping on

the surface of the water, and air drying. The dried fiber yield is approximately 5% of the weight of the green stalk.

The jute fiber ranges in color from cream white to reddish brown, changing to a dingy brown with age. When the fiber is properly extracted, it is soft and fine, with an almost silky luster. The fibers are grouped in strands 5–10 ft. long. The ultimate cells composing the fibers are 1–5 mm. long and 14–20  $\mu$  in diameter, and are blunt-pointed. Chemically, jute has a higher percentage of lignin than any other commercial soft fiber and has a lower cellulose content. This composition results in a fiber lacking in strength and durability. A chemical analysis of a typical fiber shows: hygroscopic water, 9.93%; aqueous extract, 1.03%; fat and wax, 0.39%; ash, 0.68%; lignin, 24.41%; cellulose, 63.24%.

Jute fiber is graded according to luster, softness, strength, color, cleaning, and uniformity. These characteristics vary not only according to district but also by area of growth within a district. The jute from each production center is further subgraded into as many as eight classifications. Jute fiber imported into the U.S. generally consists of the highest qualities and is bought by housemarks, the exporters' symbols of recognized prescribed qualities. Before packing and grading, the flaggy lower ends of the fiber strands that are hard and woody are cut off. These constitute the jute *cuttings* or *bulks* of commerce.

In volume and diversity of use, jute is the most important textile fiber next to cotton. It is used for burlap, sacking, backing for linoleum and rugs, webbing, twine, packing, oakum, and in a variety of products where low cost is more important than strength or durability.

**Ramie** is the fiber produced from the tall stingless nettle plant *Boehmeria nivea*.

As nearly as can be determined, the plant is native to southwestern China but will grow in any warm temperate climate. It is a plant with perennial roots, and, once growing in the proper environment, will yield at least three crops a year. The stalks, which attain a height of 5–8 ft., are cut when they begin to turn brown at the base. Unlike other bast fibers, the ramie fiber does not lend itself to the retting process.

Supplied principally by China, the fiber has been produced in small amounts in the Philippines, Europe, South and Central American countries, and in the U.S. in Florida. Satisfactory decortication, which includes separation of the fiber from the stalk and separating the fiber from the thin outer bark, is the biggest problem in the production of ramie fiber. Since China has been the principal supplier of ramie in the past, its use being confined mostly to European spinning mills, the fiber is supplied under the name of *China grass*. This consists of rather stiff greenish-yellow ribbons of adherent bark and fiber 2–5 ft. long and  $\frac{1}{2}$ –3 mm. wide, which have been peeled from the bark by hand. The ribbons from other countries are often prepared by decorticating machines. These ribbons are degummed by bacteriological or chemical processing generally involving pressure boiling. The degummed fiber yield is approximately 1% of the weight of the green plants. The term *filasse* is sometimes used to designate the long, straight, combed, degummed ramie fiber.

The degummed ramie fiber is a multiple-celled long fiber, differing from the other bast fibers in that the ultimate cells are considerably longer and thicker. The ultimate cells are  $\frac{3}{4}$ –20 in. long and 20–70  $\mu$  in diameter. The cellulose elements are arranged in spirals in the cell wall, causing the fiber to turn clockwise when moistened and allowed to dry. All other common textile fibers except flax turn counterclockwise. Degummed ramie consists of nearly pure cellulose, analysis showing 90.2% cellulose in a sample of purified ramie.

As a bast fiber, ramie is superior to all other bast fibers in strength and versatility. It has been spun, knitted, and woven, both by itself and as blends with other fibers, with very satisfactory results in the production of fabrics, laces, threads, etc.

**Sunn** is a bast fiber from the plant *Crotalaria juncea* which is cultivated on a commercial scale both in Pakistan and India. It is also known as Benares hemp from the location of the trade center for the fiber. In practically all respects, the growing, retting, and handling of the fiber parallels jute. The fiber yield is about 8% of the weight of dry stems. The fiber of commerce ranges from 3 to 6 ft. in length, with variable color from gray to brown. The fiber is variable in texture ranging from stiff and brittle to soft and silk-like, and hence is supplied in several grades depending upon the texture, color, length, and cleaning. Microscopically, the fiber is similar to true hemp (*Cannabis sativa*); it differs essentially in the presence of a very thick layer of lignin between cells. The ultimate cells are irregular in cross section, 13–50  $\mu$  in diameter. However, it is not as strong or durable as true hemp. A chemical analysis of sunn shows: hygroscopic moisture, 9.6%; water soluble, 2.6%; fats and waxes, 0.4%; ash, 0.6%; lignin, 6.4%; cellulose, 80.4%.

Sunn is used principally in the manufacture of high-quality tissue papers including cigarette paper. It is also used extensively for marine oakum and calking material and in small amounts for blending in low-price cordage and twine.

#### SEED FIBERS

**Kapok** is the seed-pod fiber of *Ceiba petandra*, a large tree growing in Indonesia, Philippines, Ecuador, and West Africa. The seed pods, spindle-shaped and 4–8 in. long, are picked from the tree, broken open, and the fibers and adherent seeds dried in an area enclosed by cotton cloth or wire netting to contain the fiber. The fiber and seeds are picked out by hand and separated by a simple air-blasting process.

The fiber has a beautiful silky luster, is almost white to yellowish brown in color, and is very light and fluffy. The fiber length ranges from  $\frac{3}{8}$  to  $1\frac{1}{8}$  in. and the diameter from 30 to 36  $\mu$ . Microscopically, the fiber resembles a smooth, transparent rod. Because of its buoyancy and moisture resistance it is used extensively for life jackets. It also finds extensive use as an insulating material in refrigeration and sound insulation. Mattresses and upholstery constitute the chief demand for the fiber. A typical chemical analysis shows: moisture, 9.9–10.0%; ash, 1.3–2.8%; cellulose, 50.3–63.6%.

Kapok is graded by district, color, and cleaning; the following Java grades are recognized: good clean prime Madura, good clean prime Porrong, good clean prime East Java, fair average quality, and fancy grade.

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FILMS, PHOTOGRAPHIC. See *Photography*.

# FILM THEORY OF FLUIDS

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Since 1844 it has been universally known that when a fluid moves over a solid surface or the surface of another fluid, a film of the moving fluid exists upon the surface of the stationary substance. The concept of this film is useful in dealing with heat and mass transfer, and its properties are controlling in various unit operations in chemical industries. Detailed applications are well illustrated under *Absorption; Distillation; Diffusion; Extraction; Heat transfer*. See also *Fluid mechanics*.

The presence of such a stationary film has been verified by a great number of scientists. The velocity distribution for a continuous and isothermal flow of a gas in a conduit is presented in Figure 1. Along the wall of the pipe, the velocity of the flow is equal to zero. As the distance from the wall increases, the flow rate becomes higher. In the neighborhood of the wall there is no other direction of flow except parallel to the wall. As the distance from the wall increases, turbulence sets in, and the flow proceeds in a forward-moving spiral with a large percentage of the fluid particles moving at right angles to the surface.

Since the "film" at the boundary travels at a very low speed, parallel to the wall with little mixing turbulence, the motion through this film at right angles to the surface must be accomplished by molecular diffusion, which is extremely slow. To simplify the engineering application of this concept, it has been assumed that the film can be visualized as a stationary part of the fluid, although all its parts move slowly along the stationary wall except those in immediate contact with it. As the flow rate of the fluid increases, the increasing turbulence will strike more deeply into the boundary film. The thickness of the assumed film is thus decreased, and any properties characteristic of the presence of this film will be affected accordingly.

Experimental explorations of the temperature and velocity across an air stream flowing turbulently in a heated pipe have been carried out (31,37,39). The distribution curves of temperature and velocity with respect to the distance from the wall, obtained thus, are very similar. It is noted that about 50% of the overall temperature drop takes place in the film whose thickness is less than 1% of the radius of the pipe. The existence of a stationary film in immediate contact with the wall is further confirmed by careful experiments with the flow of gas through very narrow capillary tubes. These experimental results agree with Poiseuille's formula which was derived from the assumption of no slip at the boundary wall.

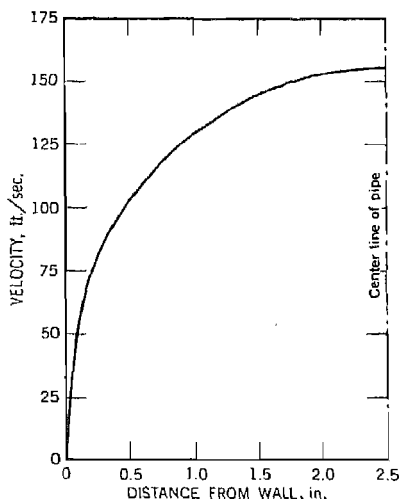


Fig. 1. Velocity distribution for isothermal flow in a circular pipe (39).

### Fluid Film in Heat Transfer

The majority of heat-transfer processes in chemical industries involve the transfer of heat between a fluid and a solid wall. Since a relatively slow-moving film exists at the boundary, heat transfer through such a film can only be accomplished by conduction, although swirling turbulence of the rest of the fluid can pick up and transfer by convection heat which has once gone through the film. Most fluids are poor heat conductors and, therefore, offer a large percentage of the resistance to heat transfer between a fluid and a solid or another fluid.

In considering the interchange of heat between a solid surface and a fluid flowing parallel to the surface, heat is assumed to be transferred from the solid surface to the fluid under steady state. To simplify the analysis of the problem, consideration is first limited to a given small portion of the surface with an interfacial area of contact equal to  $dA$ . If the temperature of the fluid at this surface is represented by  $t$ , and that of the wall by  $t_w$ , then, the rate of heat transfer,  $dq$ , from the wall to the fluid through the small area is directly proportional to both  $dA$  and  $(t_w - t)$  and can be expressed by:

$$dq = h(t_w - t)dA \quad (1)$$

where  $h$ , a proportionality constant, is defined as the film coefficient of heat transfer, which can be determined experimentally.

It might be pointed out that the temperature of the fluid must be some sort of average value whose choice, however, is rather arbitrary. Since the net effect of heat flow on a fluid in a given equipment is of primary interest, the bulk temperature that the fluid will have after complete mixing is used in equation (1).

From the mechanism of heat transfer it can be easily deduced that the coefficient,  $h$ , is a function of a large number of variables, such as the nature and shape of the surface, the rate of flow, and various physical properties of the fluid.

The heat-transfer coefficient, whose magnitude varies over a considerable range for different fluids under various flow rates, represents the thermal conductance of the fluid film. Since the capacity of heat-transfer equipment is limited by the thermal resistance of the stationary film, the heat-transfer coefficient is a controlling factor in deciding the size of the unit.

### Two-Film Concept in Mass Transfer

When a gas comes into contact with a liquid, there exists at their interface a layer of gas and a layer of liquid which are relatively free from mixing by convection. In deriving the rate equation for the mass transfer from one phase to the other, the existence of two stationary films of gas and liquid, respectively, is assumed (14,21, 33). These films are indicated as having a definite thickness, although there is no sharp demarcation between the films and the major bodies of the fluid.

In the main stream of either phase, gas or liquid, rapid mixing by convection tends to make the concentration of the solute in the fluid uniform. On the other hand, the films at the interface are free from mixing by convection; any mass transfer through them in series is accomplished only by slow molecular diffusion, which controls the overall rate of mass transfer from one phase to the other.

**Molecular Diffusion in Gases.** The fundamental differential equations for

diffusion of gases were derived by Maxwell and Stefan, who also extended them to include liquid mixtures.

Consider a binary gaseous mixture of thickness  $B_f$  containing two components,  $A$  and  $B$ , diffusing unidirectionally. The experimental evidence shows that the total frictional resistance to diffusion of  $A$  through a small distance,  $dy$ , is given by:  $\beta_{AB}\omega_A\omega_B(U_A - U_B)dy$ , where  $\omega_A$  and  $\omega_B$  are the partial molal densities of  $A$  and  $B$ ;  $U_A$  and  $U_B$  are the velocities of  $A$  and  $B$ , respectively; and  $\beta_{AB}$  is the coefficient of resistance to diffusion of component  $A$  through  $B$ . If the influence of external forces and temperature variations is negligible, a drop in the partial pressure of  $A$ ,  $-dp_A$ , must accompany its frictional resistance; therefore:

$$-dp_A = \beta_{AB}\omega_A\omega_B(U_A - U_B)dy \quad \text{or} \quad -dp_A/dy = \beta_{AB}\omega_A\omega_B(U_A - U_B) \quad (2)$$

Similarly for the component  $B$ :

$$+dp_B/dy = \beta_{BA}\omega_A\omega_B(U_A - U_B) \quad (3)$$

For the molecular diffusion the total pressure is the same at all points along the direction of diffusion:

$$p_A + p_B = \text{constant} \quad (4)$$

Differentiation of equation (4) gives:

$$-dp_A = dp_B \quad (5)$$

Dividing equation (2) by (3) after the substitution of equation (5), one obtains:

$$\beta_{AB} = \beta_{BA} = \beta \quad (6)$$

If the total pressure of the gas is low, the ideal gas law is assumed; this gives:

$$N'_A/v = \omega_A = p_A/RT \quad \text{and} \quad N'_B/v = \omega_B = p_B/RT \quad (7)$$

where  $N'_A$  and  $N'_B$  are the moles of  $A$  and  $B$ , respectively;  $v$  is the total volume of gas;  $R$  is the gas constant; and  $T$ , the absolute temperature. Representing molal rates of diffusion by:

$$dN_A/dA = \omega_A U_A \quad \text{and} \quad dN_B/dA = \omega_B U_B \quad (8)$$

Substituting equations (6), (7), and (8) into (2) and (3), gives the equation:

$$\frac{-dp_A}{dy} = \frac{dp_B}{dy} = \frac{1}{D_{AB}} \left[ p_B \frac{dN_A}{dA} - p_A \frac{dN_B}{dA} \right] \quad (9)$$

where  $D_{AB} = RT/\beta$  is the diffusivity in molal units.

Depending on the conditions of the diffusion, equation (9) can be integrated, giving the following two equations:

(1) *Gaseous diffusion of one component only (component A):*

$$\frac{-dN_A}{dA} = \frac{D_{AB}(p_{A'} - p_{At})}{B_f p_{Btm}} \quad (10)$$

(2) *Gaseous diffusion of both components in opposite directions:*

$$-\frac{dN_A}{dA} = \frac{D_{AB}(p_{Ai} - p_{Aj})}{B_f P} \quad (11)$$

where  $p_{Aj}$  and  $p_{Ai}$  are partial pressures of component A at the two sides across the gas film,  $p_{Bj}$  and  $p_{Bi}$  are the corresponding partial pressures of component B, and  $p_{B\ln}$  is the logarithmic mean of  $p_{Bi}$  and  $p_{Bj}$ .

The fundamental differential equations similar to equation (2) or (3) for the simultaneous diffusion of two gases, A and B, through a third stagnant gas, C, are:

$$-\frac{dp_A}{dy} = \beta_{AB} \frac{p_A p_B}{M_A M_B} (U_A - U_B) + \beta_{AC} \frac{p_A p_C}{M_A M_C} (U_A - U_C) \quad (12)$$

$$-\frac{dp_B}{dy} = \beta_{BA} \frac{p_A p_B}{M_A M_B} (U_B - U_A) + \beta_{BC} \frac{p_B p_C}{M_B M_C} (U_B - U_C) \quad (13)$$

Gilliland solved these equations and gave his solution in the form of two simultaneous equations (see p. 11 of ref. 38):

$$\frac{1}{D_{AC}} \frac{dN_A}{dA} + \frac{1}{D_{BC}} \frac{dN_B}{dA} = \frac{1}{B_f} \ln \frac{p_C}{p_C'} \quad (14)$$

$$\frac{dN_A}{dA} + \frac{dN_B}{dA} = \frac{D_{AB}}{B_f} \ln "A" \quad (15)$$

where "A" is equal to:

$$\left\{ \frac{\left[ \frac{(D_{AC} - D_{AB})D_{BC}}{(D_{BC} - D_{AB})D_{AC}} \right] \left[ \frac{\frac{dN_A}{dA} + \frac{dN_B}{dA}}{\frac{dN_B}{dA}} p_{Bi} \right] - \frac{\frac{dN_A}{dA} + \frac{dN_B}{dA}}{\frac{dN_A}{dA}} p_{Ai} + P \frac{(D_{BC} - D_{AC})D_{AB}}{(D_{BC} - D_{AB})D_{AC}}}{\left[ \frac{(D_{AC} - D_{AB})D_{BC}}{(D_{BC} - D_{AB})D_{AC}} \right] \left[ \frac{\frac{dN_A}{dA} + \frac{dN_B}{dA}}{\frac{dN_B}{dA}} p_{Bj} \right] - \frac{\frac{dN_A}{dA} + \frac{dN_B}{dA}}{\frac{dN_A}{dA}} p_{Aj} + P \frac{(D_{BC} - D_{AC})D_{AB}}{(D_{BC} - D_{AB})D_{AC}}} \right\}$$

Diffusion equations for a multicomponent system, although available, are even more complex and difficult to use (39). However, if the concentration of the diffusing component is small, the equations for a binary system may be used as an approximation, by considering all other gases as one stationary component.

To use the above equations, knowledge of the values of the diffusivity and the film thickness is necessary. The thickness of the film,  $B_f$ , depends upon the flow conditions and the physical properties of the gas. The value of the diffusivity, which is a function of the temperature, the molecular weights, and the molecular volumes, can be satisfactorily predicted by the equation of Gilliland and Sherwood (38).

**Molecular Diffusion in Liquids.** Similar derivations have been used to obtain the following diffusion equation for liquids:

$$-dN_A/dA = (D_l/B_l) (C_{Ai} - C_{Aj}) \quad (16)$$

where  $D_l$  = diffusivity through the liquid,  $B_l$  = thickness of the liquid film, and  $C_{A1}$  and  $C_{A2}$  = the concentration of component A at the two sides across the liquid film.

Owing to the difficulty of eliminating natural convection and the occurrence of association and dissociation in the liquid state, the present method for estimating the numerical values of the liquid diffusion coefficient is not very satisfactory. Wilke (34) developed a method for the estimation of diffusion coefficients based upon the relationships suggested by the theory of absolute reaction rates and the Stokes-Einstein equation. Correlation has been made by means of the equation:

$$F = T/\mu D_l \quad (17)$$

where  $F$  = diffusion factor, ( $^{\circ}\text{K.}$ ) (sec.)/(sq. cm.) (centipoises);  $T$  = temperature,  $^{\circ}\text{K.}$ ; and  $\mu$  = viscosity of solution, centipoises. Within the limits of available data,  $F$  is independent of the temperature for a given liquid system. For the diffusion of various solutes in a given solvent,  $F$  is a function of the molal volume of the solute. Curves of  $F$  versus the molal volume of the solute have been developed for the diffusion through water, methyl alcohol, and benzene (34). The experimentally observed data gave an average deviation of 10% from equation (17). Diffusion factors in any

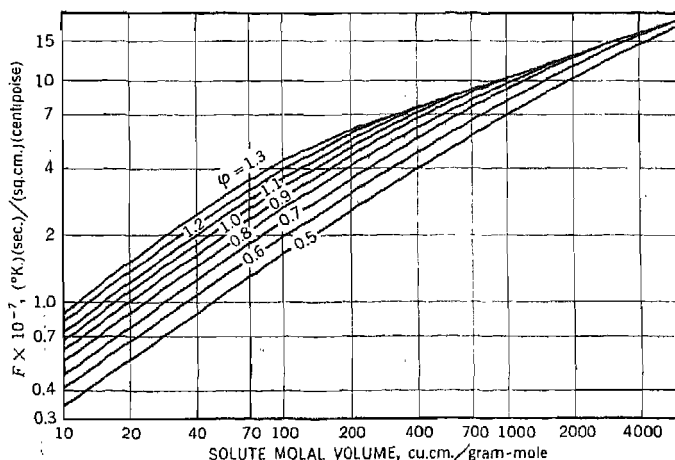


Fig. 2. Diffusion factor chart (34).

other solvent may be estimated if it is assumed that the data will correlate on a curve having a constant solvent factor,  $\phi$  (see Fig. 2). A minimum of one experimental value is necessary to characterize the solvent. When experimental data are not available, the use of a solvent factor,  $\phi = 0.9$ , is recommended.

It should be emphasized that, for the purpose of engineering design, this method can give only a first approximation of the liquid diffusion coefficient. The method is considered reasonably satisfactory for the estimation of diffusion coefficients in dilute solutions.

**Transfer Coefficient.** In evaluating the rate of a diffusional operation involving mass transfer from one phase to the other, such as gas absorption, extraction, distillation, humidification, drying, and leaching, a fictitious fluid film at the interface between two phases is usually assumed, such that the resistance of the fictitious film to molecular diffusion would be equivalent to the actual diffusional resistance from the



main body to the interface. Lewis and Whitman (14,33) were the first to advance the "two-film theory" to facilitate the design calculations for gas absorption by a solvent. With the assumption of this fictitious film, to account for the actual resistance to both molecular diffusion at the interface and eddy diffusion in the main body of the fluid, the rate of diffusion under steady state must be proportional to a driving force represented by the concentration or partial-pressure difference between the main body of the fluid and the interface. To eliminate the unnecessary difficulty in evaluating the thickness of the fictitious film and its diffusivity, all the terms other than the driving force in equations (10), (11), and (17) can be grouped together as a single constant, characteristic of the nature of the system and the conditions of the operation. This constant is defined as the transfer coefficient, and it can be easily determined by direct experiment.

In gas absorption where a liquid and a gas come into contact, the rate of mass transfer from the gas to the liquid phase, according to the foregoing discussion, can be represented by the following two equations:

$$-dN_A/dA = k_g(p_{A_g} - p_{A_i}) \quad (18)$$

$$-dN_A/dA = k_l(C_{A_i} - C_{A_l}) \quad (19)$$

where  $k_g$  = mass-transfer coefficient through the fictitious gas film, and  $k_l$  = mass-transfer coefficient through the fictitious liquid film. It should be noted that  $p_{A_g}$  is the partial pressure of component  $A$  in the main body of the gas, and  $C_{A_l}$  is its concentration in the main body of the liquid. The diffusion rate through the liquid phase is proportional to the concentration difference across the fictitious liquid film at the interface, that is, the difference in concentration between the main body of the liquid and the interface between gas and liquid. Since these surface films are very thin, the amount of solute present in them is usually negligible compared to the amount undergoing diffusion. The diffusing component which passes through one film must pass through the other, and the two films may be considered as two diffusional resistances in series. For certain systems, under certain operating conditions, the resistance offered by one film may be so small compared to the other as to be negligible.

The experimental data indicate that a substantial equilibrium exists at the liquid-gas interface, even though there may be rapid diffusion caused by high concentration gradients through the films on the two sides of that interface. Conditions at the interface are evaluated by means of two relations:

(1) *Equilibrium existing at the interface:*

$$p_{A_i} = f(C_{A_i}) \quad (20)$$

(2) *Steady-state diffusion* (the rate of diffusion through each film is equal):

$$k_g(p_{A_g} - p_{A_i}) = k_l(C_{A_i} - C_{A_l}) \quad (21)$$

The partial pressure of a component,  $p_{A_i}$ , and the corresponding liquid concentration,  $C_{A_i}$ , at the interface, can be calculated by solving equations (20) and (21), if the values of  $k_g$  and  $k_l$  are known.

Since the concentrations of the components in the main bodies of the liquid and gas can be easily determined, the equation employing an overall driving force in terms of either partial pressure or liquid concentration is frequently used to express the rate of mass transfer from gas to liquid phase, or vice versa:

$$dN/dA = K_g(p_g - p_l^*) = K_l(C_g^* - C_l) \quad (22)$$

where  $K_g$  = overall mass-transfer coefficient, with the difference of partial pressure as the driving force;  $K_l$  = overall mass-transfer coefficient, with the difference in liquid concentration as the driving force;  $p_l^*$  = partial pressure of the solute which would be in equilibrium with liquid of the composition existing in the main body of the liquid phase;  $C_g^*$  = concentration of the solute in the liquid which would be in equilibrium with the partial pressure of the solute gas existing in the main body of the gas phase. For the relationship between the overall and individual mass-transfer coefficients and the effect of solubility, see Vol. 1, p. 27.

In addition to the effect of solubility, any factor that tends to reduce the thickness of the laminar film or to increase the main body turbulence should increase the mass-transfer coefficient. For example, a high gas rate causes more rapid transfer through the gas phase, and good agitation increases the rate of transfer in the liquid.

Changes in temperature affect the transfer coefficient as well as the equilibrium relationship. Depending on the changes of turbulence, film thickness, and diffusivity, the transfer coefficients may be either increased or decreased by temperature. Available experimental data indicate that the gas transfer coefficient is not greatly changed by temperature. However, an increase in temperature usually produces a relatively large increase in the liquid transfer coefficient, due to the decrease of viscosity and the increase of turbulence which tend to aid each other in decreasing the thickness of the surface "film."

The same concept of fictitious film can be applied to mass transfer between fluids and solids. In adsorption the available data indicate that the mechanism is one of fluid-phase transfer. Since the film extends to some degree within the solid, this frequently limits the possibility of increasing the adsorption rate by using a high fluid rate, especially when the fluid film outside the solid represents only a minor part of the overall diffusional resistance.

### Velocity Distribution in Turbulent Flow

Since the temperature distribution across a flowing fluid is similar to the velocity distribution, and the heat transfer by convection can be readily determined by means of the analogy with the latter, it is important to have a sound picture of velocity distribution across the boundary layer and the core of the flowing fluid.

It has been known that the flow pattern of velocity distribution for a steady isothermal flow through a long straight pipe is different for different ranges of flow rate. With a Reynolds number,  $DG/\mu$ , less than 2100, the individual elements of fluid flow are parallel to the axis of the pipe, with no appreciable component in a radial direction. This type of flow has been defined as laminar flow. At a higher Reynolds number, a turbulent flow is obtained. For laminar flow, the velocity distribution curve follows a parabola; the ratio of the average velocity,  $V$ , to the maximum velocity,  $U_{max}$ , is  $V/U_{max} = 0.5$ . In turbulent flow, the curve rises very sharply near the wall and becomes rather flat over the greater part of the cross section of the pipe; in this case,  $V/U_{max} = 0.8$ .

The classical color-band experiments of Reynolds and later investigators suggest that a turbulent flow consists of a laminar flow near the wall, then a buffer layer, and a turbulent layer in the main body. The buffer layer, the motion of which may be either

streamline or turbulent at any given instant, has a thickness varying with time because of the periodic formation of vortices.

Figure 3 presents the velocity distribution for the isothermal flow of air in a smooth pipe based on the experimental data of Stanton. With the same large Reynolds number of 39,200, the plot of  $U/U_{max}$  versus  $y/r_0$  is the same for two sizes of pipe (1.94 in. and 2.91 in. in diameter). Later investigators determined the velocities to within 0.005 cm. of the wall and confirmed the existence of a laminar layer of flow with a velocity of zero at the wall (37).

The velocity distribution of air flowing parallel to a horizontal glass plate is shown in Figure 4. Up to a thickness of about 0.03 cm. the flow is in laminar form, since the curve in the same region on a loglog plot gives a straight line of unit slope.

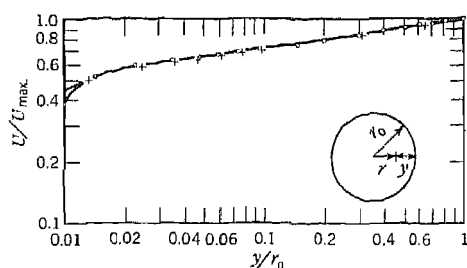


Fig. 3. Velocity distribution in smooth pipes (37).

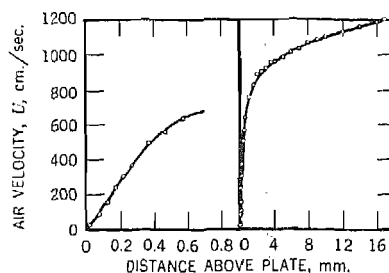


Fig. 4. Velocity distribution of air flowing parallel to a horizontal glass plate (37).

In the buffer zone from 0.3 to 1.7 mm. from the wall, the flow rate varies from 410 to 850 cm./sec. In the turbulent zone an increase of velocity of only from 850 to 1200 cm./sec. was observed. Extrapolation of the velocity in the laminar layer back to the origin indicates little slip at the plate surface.

In correlating velocity distribution for a turbulent flow in a pipe, Prandtl proposed the equation:

$$\frac{U_{max} - U}{V \sqrt{f/2}} = \frac{1}{K} \ln \frac{r_0}{y} \quad (23)$$

where  $f$  = dimensionless friction factor,  $r_0$  = the inside radius of the pipe,  $y$  = the radial distance from the pipe wall,  $K$  = a universal constant known as von Kármán's constant. Von Kármán suggested the following form (31):

$$\frac{U_{max} - U}{V \sqrt{f/2}} = \frac{1}{K} \left[ \sqrt{r/r_0} + \ln (1 - \sqrt{r/r_0}) \right] \quad (24)$$

where  $r$  = the distance of a point in the fluid from the center of the pipe. The value of  $K$  in both equations is the same and has been determined to be 0.38. The experimental data of Nikuradse for water flowing at various rates in pipes of different sizes gave fairly good agreement with both equations (23) and (24), which, however, yield a finite value for the velocity gradient at the axis, where its value should be equal to zero (31,36,37).

A universal correlation for the velocity distribution at various velocities in pipes

of different sizes and degrees of surface roughness has been proposed for three different zones:

(1) *Laminar layer:*

$$U/(V \sqrt{f/2}) = y\rho V \sqrt{f/2}/\mu \quad (25)$$

(2) *Buffer layer:*

$$U/(V \sqrt{f/2}) = -3.05 + 5 \ln (y\rho V \sqrt{f/2}/\mu) \quad (26)$$

(3) *Turbulent core:*

$$U/(V \sqrt{f/2}) = 5.5 + 2.5 \ln (y\rho V \sqrt{f/2}/\mu) \quad (27)$$

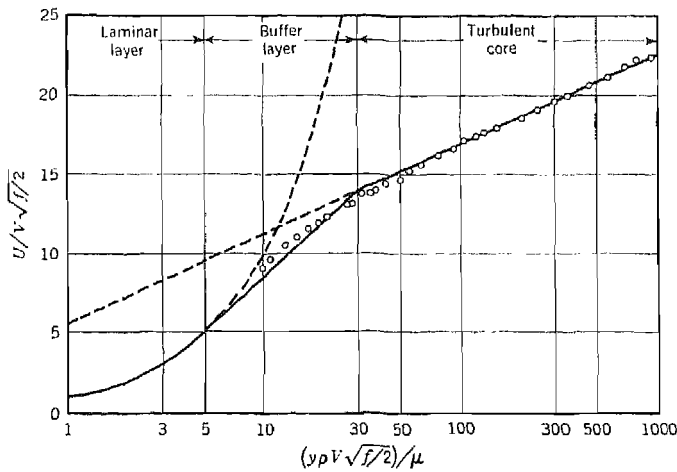


Fig. 5. Generalized velocity distribution diagram for isothermal flow of water in artificially roughened pipes (37).

These three equations can also be used to correlate the velocity distribution curve for air flow over a flat plate, the limits of the three flow zones being identified as follows:

$$(1) \text{ Laminar layer: } 0 < \frac{y\rho V \sqrt{f/2}}{\mu} < 5$$

$$(2) \text{ Buffer layer: } 5 < \frac{y\rho V \sqrt{f/2}}{\mu} < 30$$

$$(3) \text{ Turbulent core: } 30 < \frac{y\rho V \sqrt{f/2}}{\mu}$$

The close agreement of Nikuradse's data for water flow with this generalized correlation is illustrated in Figure 5.

For the isothermal flow of water in turbulent motion in vertical pipes, Koo's data agree well with the universal correlation based on Nikuradse's data. In the runs in which the water was heated, a positive deviation was noticed, when the viscosity was evaluated at a temperature of  $t_f = (t_w + t)/2$ . The agreement with the universal

correlation could be made closer by using the bulk temperature of the water to evaluate the viscosity (37).

Following the Prandtl concept of momentum transfer and a critical examination of von Kármán's formula for the velocity distribution of the turbulent flow in tubes or channels at large Reynolds numbers, a more exact formulation was developed from a study of the mixing-length distribution across the section. Although more complicated in form, the following formula has been claimed to be valid from the laminar sub-layer to the axis of the tube (32,36).

$$\frac{U_{max} - U}{V \sqrt{f/2}} = \frac{1}{0.38} \left[ \ln \frac{1 + \sqrt{1 - (y/r_0)}}{1 - \sqrt{1 - (y/r_0)}} - 2 \tan^{-1} \sqrt{1 - (y/r_0)} - \frac{1}{\sqrt{2a}} \ln \frac{1 - (y/r_0) + a + \sqrt{2a(1 - (y/r_0))}}{1 - (y/r_0) + a - \sqrt{2a(1 - (y/r_0))}} + \sqrt{\frac{2}{a}} \tan^{-1} \frac{\sqrt{2a(1 - (y/r_0))}}{a - 1 + (y/r_0)} \right] \quad (28)$$

where  $a = \sqrt{2.33} = 1.53$ . The equation is applied to both rough and smooth pipes or channels except in the immediate neighborhood of the wall. One apparent merit of the equation is that it yields a zero velocity gradient at the center of the pipe, a consistency not achieved by previous formulas.

### Analogy Between Heat and Momentum Transfer

#### TURBULENT FLOW INSIDE PIPE

**Reynolds' Analogy.** Reynolds was the first to propose the analogy between heat transfer and fluid friction (1,31,35,36,37). He stated that in geometrically similar systems there exists a simple proportion between fluid friction and heat transfer. For a flow parallel to the  $x$  axis in which the mean velocity of the fluid is a function of the  $y$  axis, Reynolds' investigation indicated that the shear stress,  $\tau$ , occurring in an arbitrary plane parallel to the  $x$  axis is equal to the momentum transferred by both molecular and turbulent exchange and is given by:

$$\tau = \mu(dU/dy) = \rho \overline{V'U'} \quad (29)$$

where  $U$  is the mean with respect to time of a local velocity, and  $\overline{U'}$  and  $\overline{V'}$  are the root mean squares of the velocity fluctuations parallel to the  $x$  and  $y$  axes, respectively. If the temperature,  $t$ , of the fluid varies with the  $y$  coordinate, the heat flow along that direction, which consists of molecular and turbulent heat transfer due to fluctuations of the velocity and temperature, can be similarly expressed by:

$$q = -k(dt/dy) + C_p \rho \overline{V't'} \quad (30)$$

where  $\rho$  = density,  $C_p$  = specific heat, and  $t'$  = fluctuation of the temperature. The first term accounts for the contribution of the eddy viscosity and the second, for the eddy conductivity. Let:

$$\overline{V'U'} = \epsilon(dU/dy) \quad (31)$$

Similarly:

$$\overline{V't'} = \epsilon(dt/dy) \quad (32)$$

where  $\epsilon$  is defined as the coefficient of the turbulent exchange. Introducing the following definitions: kinematic viscosity =  $\nu = \mu/\rho$ , thermometric conductivity =  $\kappa' = k/C_p\rho$ , equations (29) and (30) can be converted into:

$$\tau/\rho = (\nu + \epsilon)dU/dy \quad (33)$$

and

$$q/C_p\rho = (-\kappa' + \epsilon)dt/dy \quad (34)$$

If  $\nu$  and  $\kappa'$  are (a) negligible, or (b) numerically equal, the heat transfer rate is directly proportional to the shearing stress. Consider two planes,  $y = y_1$  and  $y = y_2$ , in the turbulent region where condition (a) is generally satisfied, and assume  $\tau$  and  $q$  are independent of the position of the plane, then equation (34) can be integrated into:

$$(U_2 - U_1)/\tau = C_p(t_1 - t_2)/q \quad (35)$$

This equation is known as the analytical expression of Reynolds' analogy, which also applies to the case where the variation of  $\tau$  and  $q$  with  $y$  is the same. Although in a circular pipe  $\tau$  varies linearly with  $y$ , and  $q$  depends on the velocity distribution of the fluid itself, equation (35) can be usually applied in a fully turbulent region. Condition (b) is approximately fulfilled by gases, but does not hold for most liquids, some of which may have values of  $\nu$  that are 200 times larger than  $\kappa'$ . Therefore, Reynolds' analogy may be applied to gases, not to liquids.

**Coefficient of Friction and Heat Transfer.** Two dimensionless ratios are defined as follows: coefficient of friction,  $C_f = \tau/(\rho/2)\bar{U}^2$ , and heat-transfer number,  $C_H = q/C_p\rho\bar{U}\bar{t}$ .  $\bar{U}$  is the reference velocity, the choice of which is arbitrary (for the flow through a pipe, the velocity at the center or the average velocity may be chosen);  $\bar{t}$  is the reference temperature and is usually equal to the temperature difference between two suitably chosen points in the system.

It is to be noted that  $C_H$  is the ratio between the heat flow across the stream,  $q$ , and the heat carried per unit cross-sectional area by a fluid,  $\rho C_p\bar{U}\bar{t}$ .  $C_f$  is the ratio between two stresses: shearing stress,  $\tau$ , and the dynamic pressure,  $\bar{U}^2\rho/2$ . Since the term  $\rho\bar{U}^2$  is the momentum carried by the fluid in the direction of the flow, and  $\tau$  is that transferred across the flow stream,  $C_H$  and  $C_f/2$  seem to be analogous.

**Von Kármán's Analysis** (extension of Reynolds' analogy to liquids). In the region close to the wall, that is, for  $y < \delta$ , both  $\nu$  and  $\epsilon$  cannot be negligible. By assuming  $\tau$  constant in the region where  $y \leq \delta$ , equations (33) and (34), upon integration, give:

$$U_\delta = (\tau/\rho)\int_0^\delta dy/(\nu + \epsilon) \quad (36)$$

and

$$t_w - t_\delta = (q/C_p\rho)\int_0^\delta dy/(\kappa' + \epsilon) \quad (37)$$

In the vicinity of a smooth wall, the term  $U/(\tau/\rho)^{1/2}$  is a generalized function of a parameter  $y^*$  which is equal to  $[y(\tau/\rho)^{1/2}]/\nu$ ; therefore:

$$U/(\tau/\rho)^{1/2} = f(y^*) \quad (38)$$

Differentiating equation (38) gives upon rearrangement:

$$\frac{\tau}{\rho(dU/dy)} = \frac{\nu}{f'(y^*)} \quad (39)$$

Upon substituting equation (33), equation (39) reduces to:

$$\epsilon = \nu \left[ \frac{1}{f'(y^*)} - 1 \right] \quad (40)$$

Substituting equations (39) and (40) into equation (37), one obtains:

$$U_{\delta} = \left(\frac{\tau}{\rho}\right)^{1/2} \int_0^{y_{\delta}^*} f'(y^*) dy^* \quad (41)$$

and

$$t_w - t_{\delta} = \frac{q}{C_p \rho (\tau/\rho)^{1/2}} \int_0^{y_{\delta}^*} \frac{dy^*}{(1/N_{Pr}) - 1 + (1/f'(y^*))} \quad (42)$$

The definite integral in equation (41) is a numerical constant which is assumed to be  $A'$ ; that in equation (42) is a function of  $N_{Pr}$ , represented by  $B(N_{Pr})$ . Equation (42) minus equation (41) then gives:

$$\frac{C_p \rho (t_w - t_{\delta})}{q} - \frac{\rho U_{\delta}}{\tau} = \left(\frac{\rho}{\tau}\right)^{1/2} [B(N_{Pr}) - A'] \quad (43)$$

Introducing equation (36):

$$C_H = \frac{C_f}{2} \frac{1}{1 + (C_f/2)^{1/2} [B(N_{Pr}) - A']} \quad (44)$$

Nikuradse's experimental results can be used to determine the function  $[B(N_{Pr}) - A']$ .

Introducing von Kármán's equations for velocity distribution, equations (26), (27), and (28), with the understanding that  $y^* = (y\rho V \sqrt{f/2})/\mu$ , equation (44) can be written as:

$$1/C_H = (2/C_f) + 5(2/C_f)^{1/2} \{N_{Pr} - 1 + \ln [1 + 5/6(N_{Pr} - 1)]\} \quad (45)$$

The improvement in the theory by von Kármán consists essentially of the elimination of the abrupt change in the exchange coefficient. There remains a discontinuity at the boundary between the buffer layer and the fully turbulent core; however, its effect in the calculation is rather small.

Comparison of the theoretically calculated heat-transfer coefficient with the experimental data is rather difficult for the following reasons:

(1) Most experimental investigators, in the past, did not use a calming section of sufficient length to obtain the final shape of the velocity and temperature distribution curves.

(2) The heat-transfer coefficient is a function of the physical properties which will be changed along the path during heating or cooling of the fluid by the wall.

(3) It is difficult to decide upon the right values of viscosity and density to be used in calculating the heat-transfer coefficient, since they vary over the cross section of the pipe.

(4) The interpretation of the mean temperature in the equation used for the calculation of heat-transfer coefficient is uncertain.

Eagle and Ferguson carried out experiments on the heat exchange between water and a smooth pipe wall at different temperatures, and carefully extrapolated the data to an infinitesimal temperature difference to eliminate the first three experimental difficulties. The agreement between von Kármán's theoretical values and the Eagle and Ferguson data is excellent, even though the results are not corrected for an error,

amounting to only 3 or 4% in the worst case, caused by the different interpretation of the mean temperature (1,31).

Eckert (9) employed the Zehnder-Mach interferometer for studies on the turbulent boundary layer, especially on the transition from laminar to turbulent flow. With the Reynolds number varying from  $2.71 \times 10^5$  to  $3.00 \times 10^5$ , he found good agreement between his measured temperature distribution in the laminar layer and that predicted by von Kármán's analogy.

By including the variation of  $\nu$  in the theory, and considering the thickness of the laminar layer,  $y$ , as a variable and the viscosity,  $\nu_m$ , of the fluid after  $y$  as constant at the mean temperature,  $t_m$ , Boelter and his co-workers derived the following equation with the aid of the definition of heat-transfer number (1):

$$\frac{N_{Nu}}{(N_{Re})_m(N_{Pr})_m} = \frac{\sqrt{f/2} (\Delta t_{max.}/\Delta t_{mean})}{y_1^* \left\{ (N_{Pr})_1 + \ln \left[ 1 + (N_{Pr})_m \left( \frac{30}{y_1^*} - 1 \right) \right] \right\} + \frac{2.5}{y_1^*} \ln \frac{(N_{Re})_m \sqrt{f/2}}{60} \left\{ \right.} \quad (46)$$

where  $\Delta t_{max.}$  = the difference between the temperature of the pipe wall and the maximum temperature of the fluid,  $\Delta t_{mean}$  = the difference between the temperature of the pipe wall and the average temperature of the fluid, and  $y_1^* = y(\tau/\rho)^{1/2}\delta$  at the boundary between the laminar and buffer layers. A graph of  $\Delta t_{mean}/\Delta t_{max.}$  versus the Prandtl number using the Reynolds number as parameter was prepared by Boelter (1) for use in equation (46).

Martinelli extended the analogy between heat and momentum transfer to molten metals with very low Prandtl numbers (18). For example, the Prandtl number of mercury is about 0.01. By multiplying the third term in the denominator of equation (46) by a correction factor  $1/(\gamma + 1)$  where  $\gamma$  represents the thermal resistance due to both molecular and eddy diffusion divided by the resistance due to eddy diffusion alone, the agreement obtained with the experimental data is good except for a slight scattering in the case of mercury owing to imprecision in measurement. Since Martinelli's derivation ignores the effects of heat transfer on the velocity distribution and the effects of temperature on the physical properties, it is rather surprising that his equation gives such good agreement with the experimental data.

The concept of a surface film discussed so far is one of the most venerable in both heat and mass transfer. It grows out of the analogy between heat and momentum transfer suggested by von Kármán, who calculated the numerical constants in equations (26), (27), and (28) from the experimental data of Nikuradse (19,23).

Actually, the excellent agreement of the heat-transfer data of Boelter (1) and Martinelli (18) with the theory based on the assumption of a laminar film is enough to establish the concept according to Colburn. The disagreement between Miller's and Nikuradse's work might be due to the difficulties inherent in the measurements of local velocities in the regions of large gradients.

#### TURBULENT FLOW ALONG PLANE SURFACES AND ACROSS CYLINDERS

In correlating heat-transfer data similar to Reynolds' analogy, Colburn (6) defined the heat-transfer factor,  $J_H$ , by:

$$J_H = \left( \frac{t_1 - t_2}{\Delta t_{mean}} \right) \frac{S}{A} \left( \frac{C_p \mu}{k} \right)^{2/3} = \frac{h}{C_p G} \left( \frac{C_p \mu}{k} \right)^{2/3} \quad (47)$$



Colburn pointed out that under conditions where the modified Reynolds' analogy holds,  $J_H$  is equal to  $f/2$ , but there is no such equality under other conditions.

In Figure 6 a comparison is given between heat transfer and friction for fluid flow across a single cylinder. Since the heat-transfer and friction coefficients vary markedly around the circumference, this figure is limited to the average overall effects. Apparently, there is a deviation between the friction and heat-transfer correlations. It was suggested that the turbulence set up in the air stream by the cylinder causes a large share of the drag on the cylinder, whereas only the surface friction is useful for transferring heat. The turbulence becomes disproportionally large at a high Reynolds number. To determine the possible analogy, White assumed the existence of two drags on a cylinder: skin friction, represented by the surface friction at a plane surface under the same velocity conditions; and "form drag," represented by the balance of the drag on a cylinder (6). For a turbulent flow across tubes, most of the resistance is

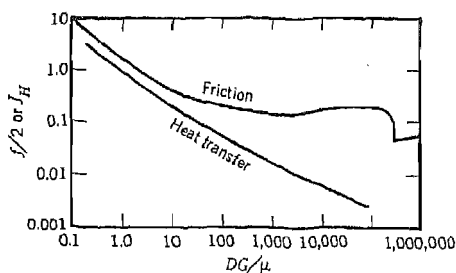


Fig. 6. Comparison between heat transfer and friction for flow of fluids across a single cylinder (6).

due to eddy turbulence which is not useful for heat transfer. It has been definitely shown that the use of a friction analogy for predicting heat transfer would be rather unsafe (5,6).

For the fluid flow over a plane surface, a remarkable agreement between friction and heat-transfer data has been found in both the viscous and turbulent region. In the turbulent region both the friction and the heat-transfer data can be represented by:

$$(h/C_p G)(C_p \mu/k)^{1/4} = R' \rho/G^2 = 0.036(LG/\mu)^{-0.2} \quad (48)$$

where  $R'$  = frictional resistance per unit surface area, and  $L$  = length of the plate in the direction of flow.

#### HEAT TRANSFER UNDER SPECIAL CONDITIONS

The previously discussed coefficient of heat transfer, which is defined as the rate of heat transfer per unit surface area per unit difference between the temperature of the surface and the mean temperature at the cross section, is substantially independent of the temperature difference except for large temperature differences (16,37). This refers to the heat transfer to or from a stream of incompressible fluid. In heat transfer to or from a stream flowing at high velocity, the value of this same coefficient is no longer independent of the temperature difference, particularly for small temperature differences. McAdams and others (16) measured heat flow to air at subsonic velocities and at substantially constant Reynolds number and found that the heat-transfer coefficient, based on the difference between the temperature of the heated wall and the bulk temperature, is not independent of this temperature difference. For a compressible fluid, they redefined the heat-transfer coefficient in terms of the difference between the surface temperature during heat transfer and the surface temperature in the absence of heat transfer, to insure that the temperature difference vanishes with the heat transfer and to preclude negative values of the coefficient. The surface temperature in the absence of heat transfer is defined as the adiabatic wall temperature,

and the corresponding coefficient of heat transfer is called the effective coefficient of heat transfer.

The adiabatic wall temperature can be determined by measuring recovery factors at the pipe wall for the adiabatic flow. The recovery factor, which is the ratio of the excess of the adiabatic wall temperature over the mean stream temperature to the excess of the stagnation temperature over the mean stream temperature, averages 0.88 and is substantially independent of the Mach number in the range from 0.2 to 1. The coefficient of heat transfer thus defined is independent of the difference between the temperature of the heated wall and the adiabatic wall temperature, according to the above-mentioned measurements, and varies with the Reynolds number substantially in the manner characteristic of turbulent flow of incompressible fluids in pipes.

An investigation of heat transfer and the associated pressure drop of sonic air flow was conducted in a range of average surface temperature up to 2060°R. and Reynolds number up to 500,000 (13). Correlation of the heat-transfer data by the conventional method, wherein the physical properties of air were evaluated at the average bulk temperature, resulted in a reduction in the Nusselt number of about 38% for an increase in average surface temperature from 610 to 2060°R. at constant Reynolds number. Satisfactory correlation of the data for the entire range of temperatures investigated was obtained, when the Reynolds number was modified by evaluating air density at the average surface temperature, and velocity at the average bulk temperature for the conventional mass flow per unit cross-sectional area. The other physical properties of air were evaluated at the surface temperature.

Similarly, when friction factors calculated from a dynamic pressure based on an average air density were plotted against the conventional Reynolds number, Humble and co-workers (10) found considerable spreading of the data with temperature level. However, if the same modified Reynolds number is used, and the friction factor is calculated from dynamic pressure based on film density, a fair correlation can be obtained.

The need for high-density heat flux in such applications as regeneratively cooled rockets, liquid-cooled aircraft engines, cyclotron targets, and continuous casting of steel prompted a recent study of high-density heat transfer from an electrically heated surface to water flowing in annuli (15). In surface boiling, the density of heat flux cannot be correlated with the total temperature change from the main body of the fluid to the heated wall by the use of the conventional heat-transfer coefficient. The experiment data can be correlated by:

$$q/A = C'(t_w - t_s)^{3.86} \quad (49)$$

where  $t_s$  = saturation temperature of gas-free water;  $C'$  is a dimensionless quantity independent of water velocity from 1 to 36 ft./sec., pressure from 30 to 90 p.s.i.a., degree of subcooling from 20 to 150°F., and dimensions of the annuli for equivalent diameters from 0.17 to 0.52 in. The value of  $C'$ , however, varies from 0.19 to 0.074, depending on the extent of degassing. High-speed Edgerton photographs indicated that surface boiling of degassed water was a two-step process involving nucleate boiling at the heated surface and condensation of the vapor in the subcooled liquid.

### Theory of Condensation

**Flow of Liquid Film on Condensing Surface.** When condensation occurs on a clean cooling surface which is wettable, a coherent and continuous film will form on the

surface, whether the surface be rough or polished. The theory of film condensation was analyzed by Nusselt, and discussed in refs. (20-24,36,37). Condensation on a vertical cooling surface produces a liquid film flowing down under the influence of gravity. The downward motion is opposed by a shearing stress due to the viscosity of the liquid. The temperature of the liquid surface in contact with condensing vapor is slightly below the saturation temperature and also decreases with decreasing wall temperature. The difference in temperature between the condensing vapor and the interface is just large enough to yield the necessary pressure difference for sending vapor to the surface. Since the poor thermal conductivity of the liquid film resists the heat flow, condensation of a film type takes place at a relatively slow rate.

Consider a surface with an angle of inclination  $\theta$  to the horizontal. As the liquid film formed by condensation flows down the surface with a velocity  $U$  at a distance  $y$  from the surface, a shearing stress which tends to retard the downward motion by gravity occurs in the liquid film and is given by the equation:

$$\tau = \mu(dU/dy) \quad (50)$$

If a mechanical equilibrium exists, the two opposing forces are in balance and the following equation is obtained:

$$d\tau = -\sin \theta dy \quad (51)$$

Combining equations (50) and (51), the final equation is then integrated to give:

$$U = -(\rho \sin \theta / 2\mu)y^2 + C_1y + C_2 \quad (52)$$

where  $C_1$  and  $C_2$  are two integration constants.

At the interface between the liquid and the condensing surface, the flow rate of the liquid is equal to zero. Substituting this boundary condition in equation (52), the latter is transformed into:

$$U = -(\rho \sin \theta / 2\mu)y^2 + C_1y \quad (53)$$

For the vapor at rest, the friction at its interface with the liquid film must be zero. At  $y = B_f$  = the thickness of the film at any point along the path of the flow,  $dU/dy = 0$ . With this second boundary condition:

$$C_1 = (\rho \sin \theta / \mu)B_f \quad (54)$$

Substitution of equation (54) into (53) gives:

$$U = -\rho \sin \theta (y^2 - 2yB_f) / 2\mu \quad (55)$$

when the vapor velocity is negligible.

If the condensing vapor flows along a surface inside a pipe of diameter  $D$  with a velocity  $V_v$ , the shearing stress on the film surface must be balanced by the pressure drop:

$$[\tau_{(y=B_f)}\pi D]dL = -(\pi/4)D^4 dp \quad (56)$$

$dp$  is the pressure drop along the direction of flow and is given by Fanning's equation:

$$dp = (2f/D)\rho_v V_v^2 dL \quad (57)$$

where  $L$  = the distance in the direction of flow of the condensate film,  $\rho_v$  = density of the vapor, and  $V_v$  = average linear velocity of the vapor flow.

Combination of equations (56) and (57) and simplification gives the shearing stress at the interface:

$$\tau_{(y=B_f)} = (f\rho_v V_v^2)/2 \quad (58)$$

Differentiating equation (53) with subsequent substitution of equations (50) and (58) gives:

$$C_1 = \pm (f\rho_v V_v^2)/2\mu + (\rho/\mu)B_f \sin \theta \quad (59)$$

The positive sign of the first term on the right-hand side is for the downward flow of the vapor, the negative sign for the upward flow.

The mean velocity of the condensed liquid film is given by:

$$V = (1/B_f) \int_0^{B_f} U dy \quad (60)$$

which, upon substitution with equations (53) and (59), is transformed into:

$$V = (\rho \sin \theta / 3\mu) B_f^2 \pm (f/2\mu)(\rho_v V_v^2/2) B_f \quad (61)$$

**Film Condensation of Vapor with Negligible Vapor Velocity.** In Figure 7 a vertical section of a water film condensing on a vertical surface is represented.  $x$  is the distance in the downward direction from the starting plane of condensation at the top. As previously pointed out, since the condensed liquid flows down the cooling surface in a laminar layer, the transfer of heat from the vapor to the cooling medium can be affected only by thermal conduction through the film. This assumption is valid provided the vapor flow rate is not high enough to change the liquid flow at its interface from streamline to turbulent. In most condensers, vapor is condensed on the outside of tubes through which the cooling medium is flowing; the vapor flow rate is usually so low that its effect on the nature of the flow of the condensed liquid is negligible. The heat balance across the laminar film of unit width gives:

$$dq = \lambda dW = k \frac{t_s - t_w}{B_f} dx \quad (62)$$

where  $\lambda$  is the latent heat of vaporization, and  $W$  is the flow rate of the liquid film along the cooling surface and is related to its average linear velocity by:

$$W = \rho B_f V \quad (63)$$

Substituting equation (61) into (63) and simplifying for the present condition of negligible vapor rate ( $V_v = 0$ ) and vertical surface ( $\sin \theta = 1$ ):

$$W = \rho^2 B_f^3 / 3\mu \quad (64)$$

Substitution of equation (64) into (62) and integration of the resulting equation gives:

$$x = \frac{\rho^2 \lambda B_f^4}{4\mu k (t_s - t_w)} + C \quad (65)$$

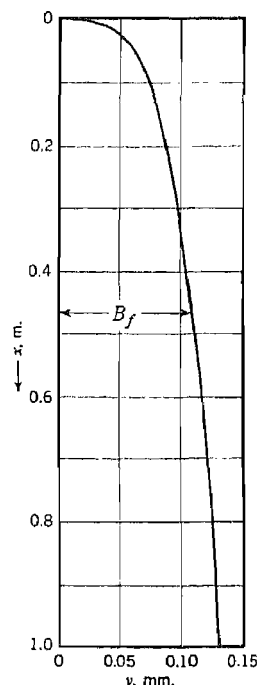


Fig. 7. Thickness of a water film on a vertical condensing surface (36).

Since  $B_f = 0$  at  $x = 0$ , the integration constant,  $C$ , in equation (65) is equal to zero. By combining equations (65) and (62) and integrating over the entire surface of height  $H$ , one obtains:

$$q = \frac{1}{3} \left( \frac{\rho^2 \lambda k^3 H^3 (t_s - t_w)^3}{4\mu} \right)^{1/4} \quad (66)$$

Since the mean transfer coefficient of the condensing vapor is defined by:

$$h_m = \frac{q}{H(t_s - t_w)} \quad (67)$$

then,

$$h_m = \frac{4}{3} \left( \frac{\rho^2 \lambda k^3}{4\mu H (t_s - t_w)} \right)^{1/4} \quad (68)$$

obtained by substituting of equation (66) into equation (67).

Equation (68) is derived on the assumption that the vapor to be condensed is a saturated one and the cooling surface is in a vertical position (36). If the condensing wall is inclined to the horizontal at an angle  $\theta$ , the average heat-transfer coefficient with negligible vapor rate is represented by the following equation after the appropriate substitution of equation (67):

$$h_m = \frac{4}{3} \left( \frac{\rho^2 \lambda k^3 \sin \theta}{4\mu H (t_s - t_w)} \right)^{1/4} \quad (69)$$

Since the thin film of the condensate on a vertical cylindrical surface represents a negligible curvature, equations (68) and (69) derived for a plane surface can also be applied to vertical cylindrical surfaces.

The theory of film condensation on a horizontal tube was advanced by Nusselt (20), who presented the following derivation (36):

Consider a point on the external surface of a horizontal tube of external diameter  $D$ . The radius from this point to the axis forms an angle  $\theta$  with a vertical line. According to equation (61), the average velocity of the liquid film flowing at this point is:

$$V = (\rho/3\mu) B_f^2 \sin \theta \quad (70)$$

The heat liberated at the interface by condensation is transferred through the laminar film of condensate by conduction. On the basis of unit length of the tube, the heat balance across the surface of arc element  $r d\theta$  on the tube surface gives:

$$\frac{k(t_s - t_w)r d\theta}{B_f} = \rho \lambda d(V B_f) \quad (71)$$

Substituting equation (70) into (71) gives:

$$\frac{3\mu k r (t_s - t_w)}{\rho^2 \lambda} d\theta = \frac{3}{4} \sin \theta dB_f^4 + B_f^4 \cos \theta d\theta \quad (72)$$

the integration of which gives:

$$B_f^4 = \frac{3\mu k r (t_s - t_w)}{\rho^2 \lambda \sin^{1/3} \theta} \left( \frac{4}{3} \int \sin^{1/3} \theta d\theta + C \right) \quad (73)$$

At the top of the tube where  $\theta = 0^\circ$ , there is no dropping of the liquid which requires that  $C = 0$  for a finite thickness of the liquid film at the top. At the bottom of the tube where  $\theta = 180^\circ$ , the numerical integration of equation (73) gives infinite thickness of the liquid film which, mathematically, indicates the dropping of the liquid from the bottom of the tube.

Similarly to the vertical plane, the mean coefficient of heat transfer on a horizontal cylindrical surface over the range  $\theta_1$  to  $\theta_2$  can be expressed by:

$$h_m = \frac{k}{\left(\frac{3\mu k r(t_s - t_w)}{\rho^2 \lambda}\right)^{1/4}} \frac{1}{(\theta_1 - \theta_2)} \int_{\theta_1}^{\theta_2} \frac{d\theta}{\psi} \quad (74)$$

where:

$$\psi = \frac{B_f^4 \rho^2 \lambda}{3\mu k r(t_s - t_w)} \quad (75)$$

If  $\theta_2 - \theta_1 = 180^\circ$ , comparison of equations (68) and (74) gives the following relation between the mean film coefficient for a horizontal cylinder and for a vertical one:

$$h_{mhor.} = h_{mvert.} 0.77(H/D)^{1/4} \quad (76)$$

Upon substitution in equation (68), the mean film coefficient for a horizontal cylinder should be:

$$h_m = 0.73 \left( \frac{\rho^2 \lambda k^3}{\mu D(t_s - t_w)} \right)^{1/4} \quad (77)$$

It may be pointed out that equation (77) can also be applied to the condensation inside a horizontal tube, provided the inside diameter is used for  $D$ .

TABLE I.

$\frac{f\rho_v V_v^2}{6\rho} \left( \frac{\rho^2 \lambda}{4\mu k(t_s - t_w)H} \right)^{1/4}$	$F \left\{ \frac{f\rho_v V_v^2}{6\rho} \left( \frac{\rho^2 \lambda}{4\mu k(t_s - t_w)H} \right)^{1/4} \right\}$
0	1.333
0.144	1.412
0.577	1.588
1.200	1.831
2.308	2.114
3.61	2.376
8.11	3.06
14.43	3.67
22.50	4.25
32.47	4.79

**Film Condensation of Vapor with Significant Vapor Velocity.** For the condensation of saturated vapor flowing downward through a vertical tube with the velocity  $V_v$ , Nusselt (20) derived the following dimensionless expression for the mean film coefficient of heat transfer:

$$h_m = k \left( \frac{\rho^2 \lambda}{4\mu k(t_s - t_w)H} \right)^{1/4} F \left\{ \frac{f\rho_v V_v^2}{6\rho} \left( \frac{\rho^2 \lambda}{4\mu k(t_s - t_w)H} \right)^{1/4} \right\} \quad (78)$$

$F$  in equation (78) represents a functional relationship, the numerical solution of which is given in Table I (20,36).

At high vapor velocity where the values in the first column are large, Jakob (36) modified equation (78):

$$h_m = \frac{3}{2} \left( \frac{f \rho \lambda k^2 p_v V_v^2}{6 \mu H (t_s - t_w)} \right) \quad (79)$$

In the turbulent range, the friction factor,  $f$ , is directly proportional to  $1/(V_v)^{1/4}$ ; the film coefficient,  $h_m$ , according to equation (79), varies with the 0.58th power of the vapor rate,  $V_v$ . Meanwhile, equation (79) indicates that the effects of vapor pressure, temperature difference across the condensate film, and surface height are more pronounced in the present case than in the case of negligible vapor velocity.

For the flow of vapor in the upward direction, Nusselt derived the equation for the film coefficient of the condensing vapor with due change of sign in the expression of vapor velocity. At a vapor rate below a certain critical value, the liquid flow divides itself into both an upward and downward direction. There occurs an unsteadiness in the thickness of the liquid film at the boundary of the two flows. For the detailed discussion refer to the original paper of Nusselt (20).

In a large condenser where a large fraction of flowing vapor is condensed along its path, the velocity of the flowing vapor changes along the condensing surface. Accordingly, the methods discussed above under the assumption of constant vapor rate have to be modified. The work in this direction has not been complete, so far. By assuming the vapor density and friction factor constant, Jakob and others extended the previous theory of condensation to the case of downward-flowing vapor with decreasing velocity. The equation developed can be applied to superheated as well as saturated vapor (36).

**Experimental Evaluation of Film Coefficient (3,13,22,23,24,36,37).** Much experimental work has been performed to evaluate the film coefficient of condensing vapor. It is interesting to compare the results calculated from Nusselt's equations with the experimental data. Such comparison is valuable because it can throw light on: (1) the soundness of the theoretical deduction, which might overlook a few important factors involved in the actual picture; (2) the reliability of a particular equipment setup; and (3) the improvement in some experimental technique in the laboratory.

Measurements of the average thickness of the liquid film (7,36,37) for an isothermal flow of liquid layers on smooth, vertical, and inclined, solid surfaces were carried out over the range of Reynolds number of 1.5 to 150,000. The assumption of laminar flow in the absence of significant vapor velocity in equation (55) was strongly supported when the Reynolds number was below 2000.

Shea and Krase measured coefficients of heat transfer on a vertical wall of different condensing heights. The mean heat-transfer coefficients measured were 10% higher for a 2.6-in. section and 30% higher for a 23-in. section than those predicted from Nusselt's equation. These deviations were explained by the formation of ripples and the presence of turbulence in the lower part of the liquid film, which is relatively thicker (36). The presence of ripples in the condensate film changes the thickness of the liquid layer from its mean value, assumed in Nusselt's theory, and yields a better overall thermal conductance through the film.

Jakob and Erk presented experimental results for condensing steam on a short vertical tube. Their results, which were lower than predicted by Nusselt's theory,

showed a 50% deviation at times. In condensing diphenyl on a vertical tube, Monrad and Badger obtained some data which were 400% higher than predicted by the theory (13,36). The major portion of experimental data on condensing vapors on vertical tubes in the published literature are higher than predicted by Nusselt's equation. This positive deviation was generally explained (6,13,36,37) by the presence of turbulence, especially along the lower part of the surface, where the condensate layer becomes thick. In addition to the change of average thickness of the liquid layer by the formation of ripples, turbulence makes the assumption of heat transfer through the liquid layer only by thermal conduction entirely invalid. For condensate under the influence of turbulence, Colburn derived the following empirical dimensionless equation for the local film coefficient of the condensate along a vertical surface (6):

$$h = 0.027 \left( \frac{C_p W}{B_f} \right) \left( \frac{4W}{g\mu} \right)^{-0.2} \quad (80)$$

This equation was derived by the use of an analogy with the case of heat transfer between a fluid and the walls of a rectangular conduit with a large ratio of width to breadth, assuming a constant temperature difference across the film. The mean coefficient of heat transfer calculated, using the mean temperature, from equation (80), showed fair agreement with the experimental results in the turbulent range for a Prandtl number of 5.

On a single horizontal tube, the experimental results generally gave better agreement with Nusselt's equation. In studying the effect of temperature, concentration of the noncondensable gas, and film temperature drop on the steam film coefficient, Othmer (21,22) maintained a constant film temperature drop along the tube by using boiling water inside the tube, and his experimental results with pure steam checked closely with Nusselt's equation.

Values smaller than the theoretical ones were obtained by Othmer *et al.* (23,24) with some alcohols, esters, and ketones; and by other investigators (3,36,37) with benzene, carbon tetrachloride, tetrachloroethylene, and toluene. Positive deviations from the Nusselt's equation have also been reported (3,4,37). On the average, the deviations from the theoretical values range from -50 to +25% in the case of a horizontal tube.

A modification of Wilson's method has been proposed and used by Chu and collaborators to eliminate the use of the thermocouple embedded in the tube wall in measuring the film coefficients of the condensing vapors (3,4). The presence of the thermocouple would probably disturb the flow of heat through the wall. The original method of Wilson is not fundamentally correct in assuming the independence of the film coefficient of the rate of heat transfer. The proposed method consists of varying the flow rate of cooling water inside the condensing tube and also the overall temperature difference, to obtain the overall heat-transfer coefficients at a constant rate of heat transfer. The overall temperature drop is varied by changing the pressure in the vapor space. The film coefficient is then calculated by the modified Wilson method at a constant rate of heat transfer. This method was applied to the measurement of the film coefficient in the condensation of benzene, toluene, ethyl acetate, bromobenzene, *n*-hexyl alcohol, nitromethane, and trichloroethylene. The experimentally measured film coefficients of the condensates at low rates of heat transfer usually gave better agreement with Nusselt's equation than at higher rates of heat transfer. This may indicate the presence of turbulence in the condensate layer at high rates of heat



transfer. With the exception of nitromethane and *n*-hexyl alcohol, the agreements of the theoretical values with the experimental ones at low rates of heat transfer are good. This suggests that the important factor in determining the discrepancy between the experimental and theoretical film coefficient of the condensates is the deviation of the condensate from the laminar flow assumed in Nusselt's equations.

Other reasons for the deviation between experimental and theoretical results are:

(1) The presence of dropwise condensation at some local points (36). The presence of this mixed condensation on a small spot, which is difficult to observe, will give a better film coefficient than predicted by the theory.

(2) High coefficients of heat transfer for most condensing vapors. This makes the temperature difference between the vapor and the condensing surface relatively small, so that its precise measurement presents considerable difficulty (19).

(3) The mechanism of drainage of the condensate from the tube. During the condensation, the liquid drops form on the tube surface and, upon growing to a sufficiently large size, drain from the tube in streams (13). In discussing the deviation of the experimental data from the theoretical ones, Othmer and Berman suggested that the assumption concerning the mechanism of drainage of the tube surface, made in the development of Nusselt's equation, should be reconsidered (23).

(4) The limited availability and accuracy of the physical properties used in evaluating the theoretical heat-transfer coefficient by Nusselt's equation. This difficulty was repeatedly pointed out by a number of investigators (3,4,23,24). For example, the experimental data for the thermal conductivity of most liquids are either available at one temperature or not at all. The data on heats of vaporization and viscosities are equally meager. Physical properties obtained by uncertain estimations or extrapolations through the necessary range of temperature would give little significance to the heat-transfer coefficient calculated from Nusselt's equation.

Nusselt's equations for the case of significant vapor velocity were checked by Jakob and others (36) using the experimental condensation of saturated and superheated steam at atmospheric pressure flowing through cooled tubes in horizontal, vertical, and various inclined positions. In general, the agreement is good.

Binary mixtures of mutually soluble components behave exactly the same in condensation as the pure compound. The film theory as previously presented can be applied to binary systems as well. However, the experimental data on the condensation of steam and ethyl alcohol scatter and deviate from the theoretical values (36).

### Mass Transfer Through a Fluid

Mass transfer through a fluid is accomplished by both eddy and molecular diffusion. The transfer across a turbulent gas stream is mainly by eddy diffusion, which is very rapid as compared with molecular diffusion. By analogy to the rate equation for molecular diffusion, one obtains:

$$-dN_A/dA = E(dC/dy) \quad (81)$$

where  $E$  is defined as eddy diffusivity.

Turbulence is in general characterized by its scale and intensity. Scale is a measure of the size of the eddies and may be defined by the length,  $L_1$ , where:

$$L_1 = \int_0^\infty R_y dy \quad (82)$$

$R_y$  in equation (81) is the correlation between two values of the velocity  $U$  at two points separated by a distance  $y$  along a line normal to the direction of flow. Within an eddy the correlation is high; if  $y$  is greater than the eddy size the two velocities are in random relation to each other, and  $R_y$  is zero (17,27).

Towle and Sherwood reported the data on the spread of carbon dioxide and of hydrogen from a point source in a turbulent air stream (30). Equation (80) was found to apply, and the eddy diffusivity obtained was approximately proportional to the Reynolds number for the flow. Since the molecular weight of carbon dioxide is twenty-two times that of hydrogen, the eddy diffusivity may be independent of the molecular weight. A study of steady-state transfer of water vapor across a 5.3-cm. gap

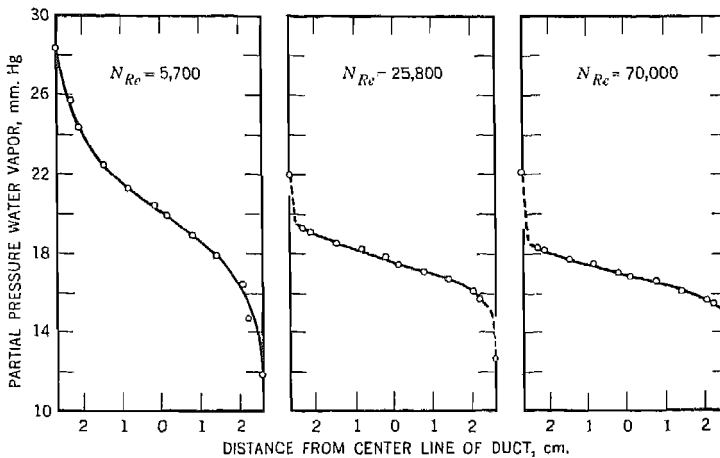


Fig. 8. Concentration traverses for steady-state diffusion of water vapor across a turbulent gas stream between two flat walls 5.3 cm. apart (27).

between parallel planes (29) indicated that the concentration gradient was linear over the main central section of the duct, and the eddy diffusivity was thus calculated by substituting the concentration traverse into equation (80). Typical concentration gradients obtained are illustrated in Figure 8. At high Reynolds numbers, the abrupt drop in concentration between the wall and the linear central section is noteworthy. The eddy diffusivity calculated agreed with those reported by Towle and Sherwood (30).

It has been pointed out that the eddy diffusivity should be proportional to the product of a mixing length and the deviating velocity in the direction of diffusion, as follows (27):

$$E = \alpha \bar{V}' l \quad (83)$$

where  $\bar{V}'$  = root mean square deviating velocity in the  $y$  direction,  $l$  = Prandtl mixing length, and  $\alpha$  = proportionality constant. Since the shear stress,  $\tau$ , in turbulent exchange (eq. 29) is given by:

$$\tau = \rho \bar{U}' \bar{V}' = \rho \bar{V}' l (dU/dy) = E (dU/dy) \quad (84)$$

and since  $\bar{U}' \bar{V}' = \epsilon (dU/dy)$ , from equation (31), it follows that:

$$E = \alpha \epsilon \quad (85)$$

The experimental data indicated that  $\alpha$  is approximately constant at 1.6, based on values of the eddy viscosity obtained from velocity traverses and friction measurements in the same duct employed in the diffusion test (29).

**The Chilton-Colburn Analogy.** Owing to the difficulties encountered in the study of diffusion and the relatively few reliable experimental data available to date, the application of the well-substantiated correlations, from the analogous process of fluid friction and heat transfer, to the test of available diffusion data and to the prediction of the diffusion rate in the absence of experimental data should prove to be desirable and convenient.

Processes involving mass transfer by diffusion are closely related to the transfer of heat, as pointed out previously. The mechanisms of heat transfer and diffusion are so similar, it would be expected that a relationship could be obtained for diffusional processes entirely analogous to that for heat transfer. In rectification, the total number of moles of material passing through the equipment remains constant and diffusion occurs in both directions. According to equations (10) and (11), the driving force in diffusion can be represented by the difference in partial pressures, and the mass-transfer coefficient is analogous to the transfer coefficient of heat. An extension of Reynolds' analogy by Chilton and Colburn led to the following equation (2):

$$\frac{(p_2 - p_1)}{\Delta p_m} \left( \frac{S}{A} \right) \left( \frac{\mu}{\rho D} \right)^{2/3} = \frac{kP}{G/M_m} \left( \frac{\mu}{\rho D} \right)^{2/3} = J_D \quad (86)$$

where  $M_m$  = mean molecular weight of the mixture and  $J_D$  = mass-transfer factor. In the equation above, a function of the ratio of viscosity to diffusivity is introduced as a term similar to  $C_p \mu / k$ , the Prandtl number, which is used in the heat-transfer correlation to account for a wide variation itself. It might be possible that the exponent of  $\mu / \rho D$  is not the same as that of the Prandtl number in the corresponding heat-transfer equation.

In other diffusional processes, such as absorption, stripping, evaporation of a liquid into a gas, or condensation of a vapor from a mixture with inert gas, the total number of moles does change as the mixture of gases passes through the equipment, and the diffusion is mainly in one direction. The corresponding mass-transfer factor for this case is represented by (2):

$$J_D = \frac{dp}{\Delta p} \frac{p_{Btm}}{p_B} \frac{S}{dA} \left( \frac{\mu}{\rho D} \right)^{2/3} = \frac{kp_{Btm}}{G/M_m} \left( \frac{\mu}{\rho D} \right)^{2/3} \quad (87)$$

where  $p_{Btm}$  = logarithmic mean of the partial pressure of the inert component,  $B$ , in the fictitious film. When the concentration of the diffusing component is small, the values of  $p_{Btm}$ ,  $p_B$ ,  $k$ , and  $G$  show little change and can be assumed constant at their respective averages. Equation (87) can therefore be integrated to give:

$$\frac{p_1 - p_2}{\Delta p_m} \frac{p_{Btm}}{p_B} \frac{S}{A} \left( \frac{\mu}{\rho D} \right)^{2/3} = \frac{kp_{Btm}}{G/M_m} \left( \frac{\mu}{\rho D} \right)^{2/3} = J_D \quad (88)$$

If the partial pressure of the diffusing component changes greatly through the equipment,  $p_{Btm}$ ,  $G$ , and  $M_m$  will vary considerably. The true mean of the driving force,  $\Delta p_m$ , is not usually equal to the logarithmic mean of its terminal values. In such a case, a graphical integration of equation (89) is used to obtain the surface area required:

$$A = \int_0^W \frac{dW}{k \Delta p} = \frac{S}{J_D} \int_1^{p_2} \frac{p_{Bm}}{p_B} \frac{dp}{\Delta p} \quad (89)$$

It might be pointed out that the equations presented here apply only to diffusion into or out of the fluid undergoing relative motion, and do not allow for any liquid film resistance.

The corresponding equation for heat transfer proposed by Colburn is of the following form (6):

$$J_H = \frac{h}{C_p G} \left( \frac{C_p \mu}{k} \right)^{2/3} \quad (90)$$

$J_H$  and  $J_D$  have been shown to be approximately equal for the same shape at the same Reynolds number (2). This relation provides a valuable connection between mass transfer and heat transfer for a wide variety of conditions.

It has been known that  $J_H$  approaches  $f/2$  for flow past streamline shapes, and may be only a small fraction of  $f/2$  for flow past vertical cylinders or bluff objects (2). The relationship between  $J_D$  and  $f/2$  has been similarly demonstrated by the experimental results from the evaporation of water from flat surfaces, cylinders, spheres, and disks placed in a turbulent air stream, and in a wetted wall tube (27). Recent work on the evaporation of liquids into turbulent gas streams made use of wetted plane surfaces, cylinders, spheres, and disks (17). Water was evaporated into air from each of the several shapes; into carbon dioxide and into helium from cylinders; benzene and carbon tetrachloride into air from cylinders; and benzene into air from spheres. The values of  $J_D$  so obtained were shown to fit remarkably well with the Chilton-Colburn analogy.

However, all the mass-transfer data previously discussed are for cases where the Schmidt number  $\mu/\rho D$  varies from 0.6 to 2.5. A recent investigation, reported by Linton and Sherwood at the 1949 Convention of the American Institute of Chemical Engineers at Pittsburgh, explored the range of Schmidt number to 1000–3000. Data on the rates of solution of benzoic acid, cinnamic acid, and 2-naphthol in the form of cast tubes, cylinders, plates, and spheres were reported to show good agreement with the Chilton-Colburn analogy prediction. This remarkable agreement can be explained by the disturbances in the transition zone between laminar and turbulent layers being propagated sidewise into the laminar layer, which is analogous to the observed boundary-layer oscillation resulting from free stream turbulence. The resulting motion normal to the pipe wall would be expected to increase mass transfer in this region. At high values of the Schmidt number the momentum diffusivity is much larger than the mass diffusivity, and mass transfer may be much more sensitive to disturbance. At low Schmidt numbers, momentum transfer should be the more sensitive. In effect, the laminar film might behave slightly turbulently.

**Analogy of von Kármán's Theory.** Following von Kármán's analogy of heat transfer in pipes, previously discussed, Sherwood (27) derived the following equation for mass transfer from a turbulent fluid to its phase boundary from equation (85):

$$-dN_A/dA = [(D/\alpha) + \epsilon] \alpha (dC/dy) \quad (91)$$

The shear stress is given by:

$$\tau/\rho = (\mu + \epsilon) dU/dy \quad (92)$$

Dividing equation (91) by (92) and assuming that  $(-dN_A/dA)/\tau$  is constant and that  $D/\alpha$  is small compared to  $\epsilon$  in the turbulent region, one obtains the following equation after integration:

$$\frac{U_2 - U_1}{\tau} = \frac{\alpha(C_1 - C_2)}{\rho(-dN_A/dA)} \quad (93)$$

where the subscripts 1 and 2 refer to any two positions in the wholly turbulent region.

By assuming a constant shear stress  $\tau_0$  through a fictitious film of thickness  $B_f$ , the integration of equation (92) gives the velocity at the film boundary,  $U_i$ :

$$U_i = \tau_0 \int_0^{B_f} \frac{dy}{(\mu + \epsilon)\rho} \quad (94)$$

Similarly from equation (91):

$$C_w - C_i = \left( -\frac{dN_A}{dA} \right) \alpha \int_0^{B_f} \frac{dy}{(D/\alpha) + \epsilon} \quad (95)$$

where  $C_i$  is the concentration of the diffusing component at the film boundary and  $C_w$  is the concentration at the phase boundary.

Substituting equation (39) into (92):

$$\mu + \epsilon = \nu/f'(y^*) \quad (96)$$

After the required variation of the eddy viscosity,  $\epsilon$ , is found by combining von Kármán's arbitrary assumption of the film boundary with equation (96), equations (94) and (95) can be integrated to give:

$$U_i = (5 + 5 \ln 6) \sqrt{\tau_0/\rho} \quad (97)$$

and:

$$\frac{\alpha(C_w - C_i)}{-dN_A/dA} = 5\sqrt{\rho/\tau_0} [\psi' + \ln(1 + 5\psi')] \quad (98)$$

where  $\psi' = \alpha\mu/\rho D$ .

If equation (98) is assumed to apply in the turbulent region, replacing  $C_i$  with the bulk concentration,  $C_0$ , and  $U_i$  in equation (97) by the average velocity,  $V$ , then combining equations (97) and (98) gives:

$$\frac{\alpha(C_w - C_0)}{-dN_A/dA} = \frac{\rho V}{\tau_0} + 5\sqrt{\rho/\tau_0} [\psi' - 1 + \ln(1 + 5\psi') - \ln 6] \quad (99)$$

whence:

$$k_c = \frac{(f/2)\alpha V}{1 + 5\sqrt{f/2}[\psi' - 1 + \ln(1 + 5\psi') - \ln 6]} \quad (100)$$

To compare this analogy of mass transfer with Gilliland's experimental data on the evaporation of a pure liquid (27) represented by the empirical equation:

$$fV/2k_c = 0.85(\psi'/\alpha)0.56 \quad (101)$$

equation (100) is transformed into:

$$fV/2k_c = 1/\alpha + 5/\alpha \sqrt{f/2}[\psi' - 1 + \ln(1 + 5\psi') - \ln 6] \quad (102)$$

with  $\alpha = 1.6$ , as found by Sherwood and Woertz (29).

Figure 9, which plots  $fV/2k_c$  versus  $\mu/\rho D$  for a Reynolds number of 10,000, illustrates the comparison of Chilton-Colburn's and von Kármán's analogy with Gilliland's experimental data. These data were obtained with a variety of liquids: water, toluene, aniline, ethyl acetate, chlorobenzene, and various alcohols, which gave no significant differences. The von Kármán analogy as represented by equation (102) is seen to be in excellent agreement with the experimental data. This is due to the inclusion of a factor,  $\alpha$ , which is not used in the original theory of von Kármán.

The same general reasoning, which has been used to eliminate many of von Kármán's original assumptions, can be followed in deriving the following theoretical equation for the steady-state mass transfer across a turbulent stream flowing between two parallel plates:

$$\frac{V\Delta C}{-dN_A/dA} = \frac{N_{Re}}{2\alpha} \ln \frac{N_{Re}\sqrt{f}}{N_{Re}\sqrt{f} - 28.2} - \frac{\mu}{2\beta'\alpha} \left( \frac{169}{N_{Re}\sqrt{f}} - 1 \right) + \frac{2.82}{\alpha q\sqrt{f}} \ln \frac{(60p + 0.2 - q')(10p + 0.2 + q')}{(60p + 0.2 - q')(10p + 0.2 - q')} \quad (103)$$

where:

$$\beta' = \frac{(\mu + \epsilon)}{N_{Re}}, \quad p = \frac{-1.13}{N_{Re}\sqrt{f}}, \quad \text{and } q' = \left[ \frac{1}{25} + \frac{4.51}{N_{Re}\sqrt{f}} \left( \frac{1 - \psi'}{\psi'} \right) \right]^{1/2}$$

The comparison of this equation with the experimental data for carbon dioxide, air, and helium indicates a good general agreement, with the exception of air at high Reynolds number. Since von Kármán's main assumptions were eliminated in deriving equation (103), the results may lend further support to the general concept on which von Kármán's analogy is based (27,28).

### Nomenclature

$A$	Surface area at right angle to heat flow, sq.ft.
$A'$	Numerical constant
$B_f, B_l$	Thickness of gas and liquid film, respectively, ft.
$B(N_{Pr})$	Function of Prandtl number
$C$	Concentration, lb.-moles/cu.ft.
$C'$	Dimensionless quantity
$C_f$	Coefficient of friction, dimensionless
$C_H$	Heat-transfer number, dimensionless
$C_p$	Specific heat at constant pressure, B.t.u./[lb.](°F.)
$C_w$	Concentration at the wall, lb.-moles/cu.ft.
$D$	Gas diffusivity, lb.-moles/(ft.)(hr.)
$D_l$	Liquid diffusivity, lb.-moles/(ft.)(hr.); $D_l$ in equation (17) has the units sq.cm./sec.
$E$	Eddy diffusivity, sq.ft./hr.

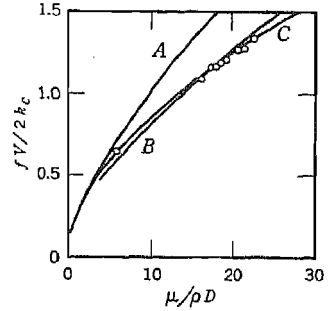


Fig. 9. Comparison of various analogies with data on vaporization in a wetted-wall column at  $N_{Re} = 10,000$ : curve A, Chilton-Colburn; curve B, von Kármán; curve C, Gilliland (empirical) (27).

$F$	Diffusion factor, $(^{\circ}\text{K.})(\text{sec.})^2/(\text{cm.})(\text{gram})$
$f$	Friction factor, dimensionless
$G$	Mass velocity, $\text{lb.}/(\text{hr.})(\text{sq.ft.})$
$g$	Gravitation constant, $\text{ft.}/\text{sec.}^2$
$H$	Height of the surface, ft.
$h$	Coefficient of heat transfer, $\text{B.t.u.}/(\text{hr.})(\text{sq.ft.})(^{\circ}\text{F.})$
$J_D$	Mass-transfer factor, dimensionless
$J_H$	Heat-transfer factor, dimensionless
$K$	Von Kármán's constant
$K_g$	Overall mass-transfer coefficient of gas film, $\text{lb.-moles}/(\text{hr.})(\text{sq.ft.})(\text{atm.})$
$K_L$	Overall mass-transfer coefficient of liquid film, $\text{lb.-moles}/(\text{hr.})(\text{sq.ft.})(\text{lb.-moles}/\text{cu.ft.})$
$k$	Thermal conductivity, $\text{B.t.u.}/(\text{hr.})(\text{sq.ft.})(^{\circ}\text{F.}/\text{ft.})$
$k_g$	Mass-transfer coefficient of gas film, $\text{lb.-moles}/(\text{hr.})(\text{sq.ft.})(\text{lb.-moles}/\text{cu.ft.})$
$k_g$	Mass-transfer coefficient of gas film, $\text{lb.-moles}/(\text{hr.})(\text{sq.ft.})(\text{atm.})$
$k_L$	Mass-transfer coefficient of liquid film, $\text{lb.-moles}/(\text{hr.})(\text{sq.ft.})(\text{lb.-moles}/\text{cu.ft.})$
$L$	Length of flow in the direction of flow, ft.
$l$	Prandtl mixing length, ft.
$M$	Molecular weight
$N$	Rate of diffusion, $\text{lb.-moles}/\text{hr.}$
$N'$	Pound-moles of gas
$N_{Nu}$	Nusselt number, $hD/k$
$N_{Pr}$	Prandtl number, $C_p\mu/k$
$N_{Re}$	Reynolds number, $DV\rho/\mu$
$P$	Total pressure, atm.
$p$	$-1.13/N_{Re}\sqrt{f}$
$p_A, p_B$	Partial pressure of $A$ and $B$ , respectively, at any point in the gas, atm.
$p_A', p_{A_s}$	Partial pressures of $A$ at the boundary of a film, atm.
$p_B', p_{B_s}$	Partial pressure of $B$ at the boundary of a film, atm.
$p_{B\ln}$	Logarithmic mean of partial pressure of $B$
$p_{Ag}$	Partial pressure of gas in the main body of the gas stream, atm.
$q$	Rate of heat transfer, $\text{B.t.u.}/\text{hr.}$
$q'$	$\sqrt{1/25 + (4.51/N_{Re}\sqrt{f})}[(1 - \psi')/\psi']$
$R$	Ideal gas constant, $(\text{atm.})(\text{cu.ft.})/(\text{lb.-moles})(^{\circ}\text{R.})$
$R'$	Frictional resistance per unit area, $\text{lb.}/(\text{ft.})(\text{hr.})^2$
$R_y$	Correlation between two values of the velocity, dimensionless
$r$	Local radius, ft.
$r_0$	Total radius, ft.
$S$	Cross-sectional area, $\text{sq.ft.}$
$T$	Bulk temperature in absolute scale, $^{\circ}\text{R.}$
$t$	Bulk temperature, $^{\circ}\text{F.}$
$\bar{t}$	Reference temperature, $^{\circ}\text{F.}$
$t'$	Temperature fluctuation, $^{\circ}\text{F.}$
$t_f$	Film temperature, $(t_w + t)/2$ , $^{\circ}\text{F.}$
$t_s$	Saturation temperature, $^{\circ}\text{F.}$
$t_w$	Wall temperature, $^{\circ}\text{F.}$
$t_\delta$	Temperature at a distance $\delta$ from the wall, $^{\circ}\text{F.}$
$\Delta t_{max.}$	Difference between the temperature of the pipe wall and the maximum temperature of the fluid, $^{\circ}\text{F.}$
$\Delta t_{mean.}$	Difference between the temperature of the pipe wall and the average temperature of the fluid, $^{\circ}\text{F.}$
$U$	Local linear velocity, $\text{ft.}/\text{hr.}$
$\bar{U}$	Reference velocity, $\text{ft.}/\text{hr.}$
$U'$	Velocity fluctuation parallel to $x$ axis, $\text{ft.}/\text{hr.}$
$U_s$	Linear velocity at the film boundary, $\text{ft.}/\text{hr.}$
$U_{max.}$	Maximum velocity, $\text{ft.}/\text{hr.}$
$U_\delta$	Linear velocity at a distance $\delta$ from the wall, $\text{ft.}/\text{hr.}$
$u$	Mass rate of fluid flow, $\text{lb.}/\text{hr.}$

$V$	Average velocity, ft./hr.
$\overline{V^2}$	Root mean square velocity in $y$ direction, ft./hr.
$V_v$	Vapor velocity in the condenser, ft./hr.
$W$	Rate of flow of a liquid film, lb.-moles/hr.
$y$	Distance along the path of the diffusion or heat transfer, or radial distance from the pipe wall, ft.
$y^*$	$y \sqrt{\tau/\rho/\nu}$
$\alpha$	Constant, dimensionless
$\beta$	Coefficient of diffusion resistance, (atm.)(ft.)(hr.)/(lb.-moles) <sup>2</sup>
$\beta'$	$(\mu + \epsilon)/NRe$
$\delta$	Distance from the wall (close to the wall), ft.
$\epsilon$	Coefficient of turbulence, sq.ft./hr.
$\theta$	Angle of inclination to the horizontal
$\kappa$	Thermometric conductivity, (lb.-moles)(°F.)(ft.)(hr.)(B.t.u.)(lb.-moles/cu.ft.)
$\lambda$	Latent heat of vaporization, B.t.u./lb.
$\mu$	Viscosity, lb./(hr.)(ft.); centipoise in equation (18)
$\nu$	Kinematic viscosity, $\mu/\rho$ , sq.ft./hr.
$\nu_m$	Kinematic viscosity at the mean temperature, sq.ft./hr.
$\rho$	Density, lb./cu.ft.
$\rho_v$	Density of vapor in the condenser, lb./cu.ft.
$\tau$	Shear stress, lb./sq.ft.
$\tau_0$	Shear stress in a fictitious film, lb./sq.ft.
$\varphi$	Solvent factor
$\psi$	$B_{fp}^2 \lambda / 3 \mu \kappa r (t_s - t_w)$
$\psi'$	$\alpha \mu / \rho D$
$\omega$	Partial molal density, lb.-moles/cu.ft.

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JU CHIN CHU

**FILTERS, LIGHT.** See *Colorimetry and fluorimetry*, Vol. 4, p. 271.

### FILTRATION

Filtration is the operation of separating more or less completely a heterogeneous mixture of a fluid and particles of solid. The separation is accomplished by means of a filter medium such as a screen, cloth, or porous bed, which permits the flow of the fluid but retains the solid particles. The fluid may be a liquid such as water or a gas such as air. The solid particles deposited on the filter medium produce a porous bed or filter cake, through which the fluid or filtrate flows. The fluid is caused to flow by various means: gravity, pressure, vacuum, or centrifugal force (for centrifugal filters see *Centrifugal separation*). The principal resistance to flow is usually created by the porous filter cake. Therefore, filter calculations are based upon the relationships for flow through porous mediums, with modifications to include the resistance of the filter mediums and equipment.

The variety of methods of creating a driving force for flow and the different methods of cake deposition, cake removal, and filtrate removal result in a great variety of filter equipment. This equipment will be described after discussion of the basic theory.

#### Theory of Filtration

##### THEORY BASED ON PERMEABILITY AND A RIGOROUS MATERIAL BALANCE

Henri Darcy is credited with originally describing (in 1856) the relationship for

flow through filter beds. His equation, modified to include the viscosity term, is given in equation (1):

$$v = \frac{1}{A} \frac{dV}{dt} = \frac{K(-\Delta P_c)}{L\mu} \quad (1)$$

where  $v$  = velocity based on total area, cu.ft./(sq.ft.)(sec.);  $t$  = time, sec.;  $V$  = volume of filtrate, cu.ft.;  $A$  = area of filter medium, sq.ft.;  $L$  = thickness of filter cake, ft.;  $K$  = permeability, a property of the filter cake, cu.ft./sec.<sup>2</sup>;  $\Delta P_c$  = pressure drop across the filter cake, lb./sq.ft.; and  $\mu$  = viscosity of filtrate, lb./(sec.)(ft.). Equation (1) may be used to describe the flow of a clear fluid through a porous medium, as, for example, water through sand. The permeability,  $K$ , is a constant for beds of hard crystalline or granular materials and may be evaluated by a simple flow measurement. However, in all filters, solid particles are deposited over a period of time, thereby increasing the resistance to flow and causing a decrease in filtering rate. Nevertheless, equation (1) may be used to describe the flow through a filter cake at any particular instant, and the equation may be integrated over a given filter cycle. To make this integration, it is necessary to express the variable  $L$  as a function of either  $V$  or  $t$ , which is accomplished through a material balance between the solids in the cake and the solids in the slurry. The mass of solids in the cake equals the mass of solids originally in the slurry.

$$(1 - X)LA\rho_s = (V + XLA)\rho x/(1 - x) \quad (2)$$

where  $X$  = porosity of cake, volume of void space/total volume of cake;  $XLA$  = volume of fluid in cake;  $x$  = mass fraction solids in feed slurry;  $\rho$  = density of filtrate; and  $\rho_s$  = density of solids in cake. Solving equation (2) for  $V$  and differentiating:

$$dV = \frac{\rho_s(1 - x)(1 - X) - \rho xX}{\rho x} A dL \quad (2a)$$

Substituting the value of  $dV$  from equation (2a) in equation (1):

$$dt = \frac{\rho_s(1 - x)(1 - X) - \rho xX}{\rho x} \frac{\mu L dL}{K(-\Delta P_c)} \quad (3)$$

For a given slurry, the variables of equation (3) are the pressure drop,  $\Delta P_c$ , the cake thickness,  $L$ , the time,  $t$ , the porosity of the cake,  $X$ , and the permeability of the cake,  $K$ . For the ideal case of a "noncompressible cake," the porosity and permeability are also constants. These constants may be grouped as follows:

$$C_L = [\mu/2K\rho x][\rho_s(1 - x)(1 - X) - \rho xX] \quad (4)$$

Equation (5) is obtained by substituting equation (4) in equation (3):

$$\int dt = \int \frac{C_L 2L dL}{(-\Delta P_c)} \quad (5)$$

For a constant-pressure filtration,  $\Delta P_c$  is constant and equation (5) may be integrated:

$$t = C_L L^2/(-\Delta P_c) \quad (6)$$

A similar procedure, in which equation (2) is solved for  $L$  and substituted in equation (1), gives the relationship between time and filtrate volume:

$$t = C_v V^2 / A^2 (-\Delta P_c) \quad (7)$$

in which:

$$C_v = \frac{\mu \rho x}{2K[\rho_s(1-x)(1-X) - \rho x X]} \quad (8)$$

For a given slurry, and when the assumption of uniform conditions of cake, filtrate, and slurry can be made, the value of  $C_v$  or  $C_L$  may be computed from the available operating data and used to estimate other operating conditions, even though the variables, such as permeability and porosity, are unknown.

#### THEORY BASED ON SPECIFIC RESISTANCE AND RATIO OF CAKE TO FILTRATE

A somewhat different approach to the problem of filtration is the concept that the rate of filtration is directly proportional to a driving force and inversely proportional to a resistance. This concept has furnished the basis for most of the literature on filtration (4,12,16,19,20,23,24,25). In developing the equation based on this concept a material balance is made, similar to equation (2):

$$(1-X)LA\rho_s = V\rho r \quad (9)$$

where  $r$  = the mass ratio of dry cake to total filtrate. Solving equation (9) for  $L$  and substituting in equation (1):

$$\frac{dV}{dt} = \frac{A^2 K \rho_s (1-X)}{V r \rho \mu} (-\Delta P_c) \quad (10)$$

The expression  $K\rho_s(1-X)$  represents the specific conductance of the filter cake. The reciprocal of this quantity is termed the specific resistance  $\alpha$  or:

$$\alpha = 1/K\rho_s(1-X) \quad (11)$$

Substituting equation (11) in equation (10) and integrating for constant-pressure filtration:

$$V^2 = 2A^2 t (-\Delta P_c) / \alpha r \rho \mu \quad (12)$$

Equation (13) is the equivalent of equation (8), and a comparison shows that the filtration constant  $C_v$  is related to the specific resistance  $\alpha$  as follows:

$$C_v = \alpha r \rho \mu / 2 \quad (13)$$

#### RESISTANCE OF FILTER MEDIUMS AND FILTER LINES

All of the previous equations express the relationships when the pressure drop across the cake,  $\Delta P_c$ , is known. However, in most commercial filters this pressure drop is not known, but instead the pressure drop across the filter cake, the filter medium, and the lines is the only pressure that can be measured. The previous equations must be modified to include the additional resistance of the filter medium and lines between the points at which the pressure drop is measured. This resistance can be expressed as "equivalent cake thickness,"  $L_e$ , or "equivalent volume of filtrate,"  $V_e$ , to produce a cake of the equivalent thickness  $L_e$ .

Using the total pressure drop,  $\Delta P$ , equation (5) is rewritten as follows:

$$\int dt = \int \frac{C_L 2(L + L_e) d(L + L_e)}{(-\Delta P)} = \int \frac{C_L 2(L + L_e) dL}{(-\Delta P)} \quad (14)$$

The time of run is  $t$  and is zero when the filtration begins;  $L$  is thickness of cake at time  $t$ :

$$\int_0^t dt = \int^L \frac{C_L 2(L + L_e) dL}{(-\Delta P)} \quad (15)$$

For constant-pressure filtration with  $L_e$  constant:

$$t = C_L(L^2 + 2LL_e)/(-\Delta P) \quad (16)$$

Similarly, for constant-pressure filtration with  $V_e$  constant:

$$t = C_v(V^2 + 2VV_e)/A^2(-\Delta P) \quad (17)$$

Equations (16) and (17) are rigorous for the constant-pressure filtration of noncompressible cakes when  $L_e$  or  $V_e$  are constants.

#### COMPRESSIBLE CAKES

Strictly speaking, the ideal case of a noncompressible cake never exists. However, most cakes composed of crystalline or granular materials in which the particle size is coarser than 200 mesh are so slightly compressible that the previous equations may be used for engineering calculations without further modification. Other filter cakes, particularly those composed of flocculent precipitates, are highly compressible, especially in instances where a large pressure drop is used.

One method of modifying the previous equations for use with compressible cakes is to determine experimentally the permeability and porosity as a function of pressure gradient. Instantaneous values of these quantities may be substituted in differential equation (3) and the equation may be integrated graphically. A more convenient but approximate method of handling compressible cakes is that of expressing the filtration constant,  $C_v$ , or specific resistance as a function of the pressure drop raised to a power:

$$C_v = C'_v(-\Delta P)^a \quad (18)$$

or:

$$\alpha = \alpha'(-\Delta P)^a \quad (19)$$

where  $\alpha'$  and  $a$  are constants for a particular cake, and  $C'_v$  is constant for a particular slurry. Similarly a correction for the resistances of the filter medium and connections may be expressed as:

$$2C_e V_e = 2c(-\Delta P)^b \quad (20)$$

or:

$$V_e \alpha = \beta(-\Delta P)^b \quad (21)$$

Substituting equations (18) and (20) in the differential form of equation (17):

$$\frac{dt}{dV} = \frac{2C_v V}{A^2(-\Delta P)^{1-a}} + \frac{2c}{A^2(-\Delta P)^{1-b}} \quad (22)$$

The integrated equations become:

$$t = \frac{C'_v V^2}{A^2(-\Delta P)^{1-a}} + \frac{2cV}{A^2(-\Delta P)^{1-b}} \quad (23)$$

or:

$$t = \frac{r\rho\mu V}{2A^2(-\Delta P)} [\alpha'(-\Delta P)^a V + 2\beta(-\Delta P)^b] \quad (24)$$

In the equations above,  $\alpha'$ ,  $a$ ,  $\beta$ , and  $b$  are constants for a particular cake, and  $C'_v$  and  $c$  are constants for a particular slurry. These constants must be evaluated experimentally.

#### FILTER AIDS

Compressible particles such as the precipitate particles of hydroxide sludges and organic slimes tend to deform plastically under the influence of a pressure gradient so as to fill the voids between particles. This is a serious phenomenon in filtration, because the permeability approaches zero as the porosity approaches zero, and filtration ceases. Even slight changes in porosity have a pronounced effect on the permeability of the filter cake, the latter varying approximately as the 4th to the 6th power of the porosity.

Filter aids are often used to overcome this undesirable decrease in porosity. Filter aids consist of solid particles which produce relatively noncompressible and porous cakes. Materials such as kieselguhr or diatomite, asbestos fibers, pulverized bone black, calcium carbonate, calcium sulfate, and sawdust flour are examples of materials used as filter aids. Some of these materials also serve as decolorizing agents.

In general, the material which produces the most porous cake without appreciable compressibility is the best filter aid. By this criterion, diatomite is superior to calcium carbonate because the minute spiny skeletons constituting diatomite form a rigid meshwork which is comparatively noncompressible. Also, the porosity of diatomite is usually 10-20% greater than that of crystalline materials such as calcium carbonate. However, the process may control the selection of the filter aid. In the treatment of waste "pickle liquor" from steel mills the liquor may be neutralized with lime to form a precipitate composed essentially of calcium sulfate and ferrous hydroxide. The calcium sulfate acts as a filter aid and makes it possible to filter the gelatinous hydroxide.

If a filter aid is added mechanically to improve filtration it may be added as a precoat or may be mixed with the slurry. In filtering raw sugar liquors, about 1 lb. of diatomite is added for each 100 sq.ft. of filter area.

#### INTERPRETATION OF FILTRATION DATA

The performance of any filter is very sensitive to the variables of filtration; that is, slight changes in these variables cause major changes in the filter operation. For the simple case of filtration of crystalline or granular noncompressible solids, a very small per cent increase in fines may halve the permeability (or double filter resistance) with a corresponding decrease in filter capacity. Although it is possible to estimate a value of permeability from average particle size, porosity, and particle shape, the sensitivity of this variable makes it desirable to evaluate experimentally the permeability or filtration constants,  $C_L$  or  $C_v$ , by tests on the slurry to be filtered. For this case a simple flow measurement generally suffices.

If the filter cake is compressible, as is the case with most flocculent precipitates, the filtration constants also vary with the pressure used, and a series of experimental tests taken at different pressures is required.

Values of the filtration constant  $C_v$  may be calculated from the data of these tests, and the quantity  $-\Delta P/C_v$  may be plotted versus the pressure drop,  $-\Delta P$ . For non-compressible cakes,  $C_v$  is independent of pressure and the plot results in a straight line having a slope of  $1/C_v$  and passing through the origin. If the cake is compressible,  $C_v$  will increase with  $-\Delta P$  to produce a curved line which may have a maximum. The value of  $-\Delta P$  at the maximum is the pressure drop which will give maximum capacity when filtering the particular slurry. Data on compressible cakes may be analyzed further by plotting equation (18) on logarithmic coordinates. The slope of the line is the exponent  $a$  and the intercept at  $-\Delta P = 1$  is  $\log C'_v$ . A similar plot of equation (20) may be used to evaluate the exponent  $b$ . In this case the intercept is  $\log 2c/4$ . Values of  $a$  range from zero for noncompressible cakes to 0.15 for calcium carbonate and kieselguhr, up to a maximum of about 0.9 for compressible hydroxide sludges. Values of  $b$  are of the same order of magnitude and a simplified approximate equation results when  $a$  is substituted for  $b$  in equation (23).

The theoretical relationships for predicting air flows for continuous filters are particularly useful. The vacuum equipment for continuous vacuum filters usually accounts for an appreciable portion of the initial and operating costs. For economical operation it is important that this equipment be selected correctly. In the past, estimation of the correct blower equipment has been a difficult problem and in many installations it has been necessary to change this equipment after putting the filter into operation.

Air flow during dewatering represents an unsteady state for a batch operation. Air velocities determined experimentally on a batch-test filter must be graphically integrated over the desired time cycle to predict the accumulative air flow. Direct measurements can be made on a laboratory continuous filter, but for satisfactory testing an appreciable quantity of slurry is required. Recycling the test slurry reduces the quantity of slurry required, but continued recycling usually causes a change in the properties of the slurry, such as an increase in percentage of fines and crystal growth. Such changes may make tests on recycled slurries unreliable. For these reasons it is often more satisfactory to determine the cake porosity, permeability, and residual saturation by simple laboratory measurements. With these data, cake deposition, air flows, degree of dewatering, and results of washing may be calculated for different conditions of vacuum, cake thicknesses, cycle time, etc. Such calculations make it possible to analyze the combined effects of the many variables other than by an extensive series of laboratory tests. After an analysis it may be advisable to make a final experimental test as a check.

In many operations such variables as particle size and slurry composition are difficult or impossible to control. In these cases the filter must be designed with considerable flexibility. Rotary filters for such services generally employ variable drive and submergence.

#### FILTRATE REMOVAL BY AIR FLOW

After the filter cake is formed, a major portion of the filtrate in the voids of the cake may be removed by passing air through the cake. This procedure is termed "dewatering" and involves the nonsteady-state flow of two phases, filtrate and air (2).

In dewatering, the flow of the two phases depends upon the volumetric proportion of filtrate and air in the voids of the cake. The volumetric ratio of filtrate to voids, termed the saturation,  $S$ , is used to describe the proportions of these two phases.

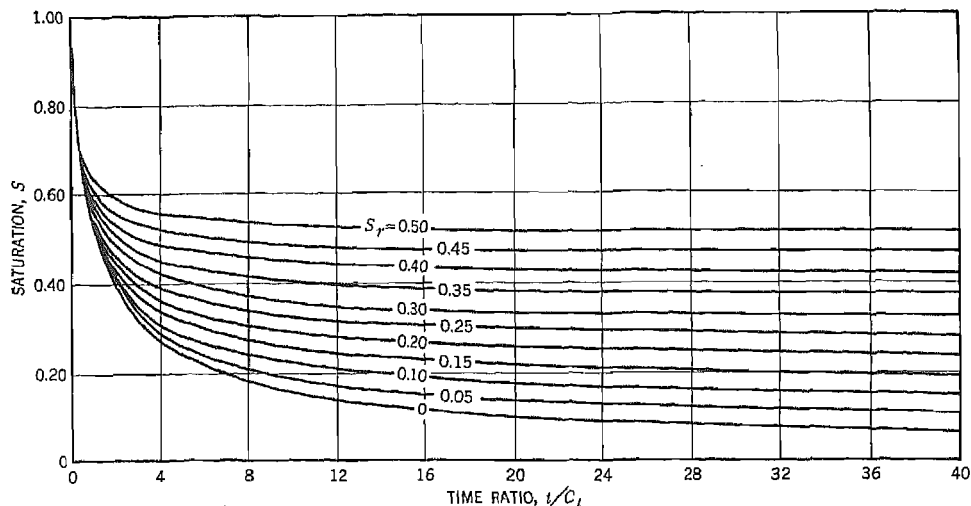


Fig. 1. Dewatering curve (low range) (1).

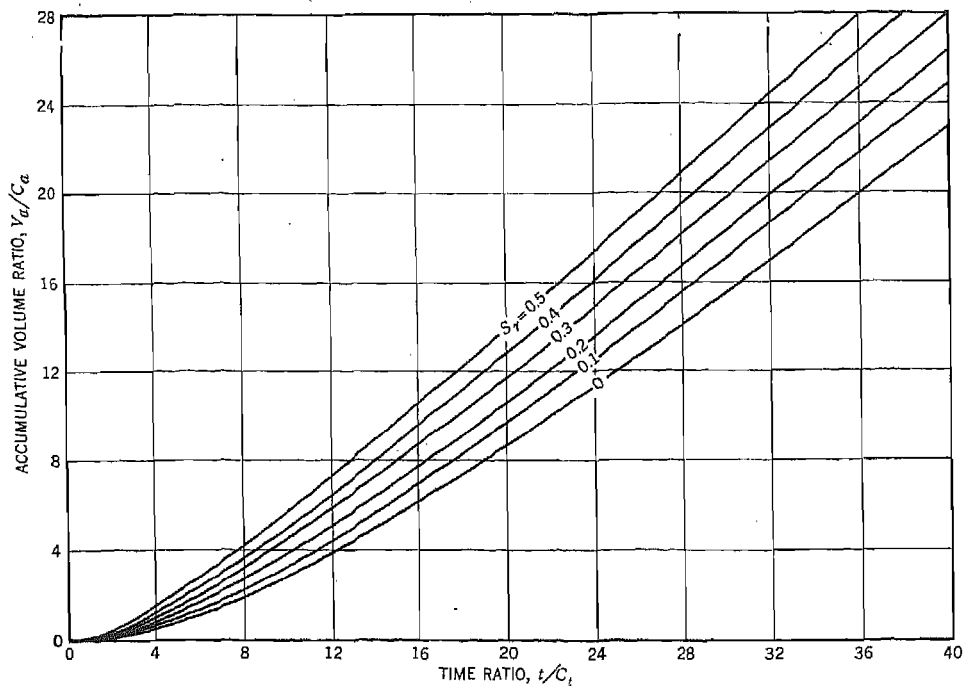


Fig. 2. Integrated air-rate curve (low range) (1).

Capillary forces in the cake prevent the complete removal of the filtrate by fluid flow alone. Further removal may be accomplished by washing the cake and/or drying it with hot air. The filtrate held in the cake by capillary forces is termed the residual

saturation,  $S_r$ . The value of the residual saturation depends upon the size of the voids in the cake, the pressure gradient, and the surface tension of the filtrate. It should be evaluated experimentally; however, the following equation may be used as an approximation:

$$S_r = 0.025[gL\gamma/K(-\Delta P_c)]^{0.264} \quad (25)$$

where  $\gamma$  = surface tension of filtrate, lb./ft.; and  $g$  = gravitational constant, 32.17 ft./sec.<sup>2</sup>. In dewatering, the saturation decreases from unity to some lesser value,

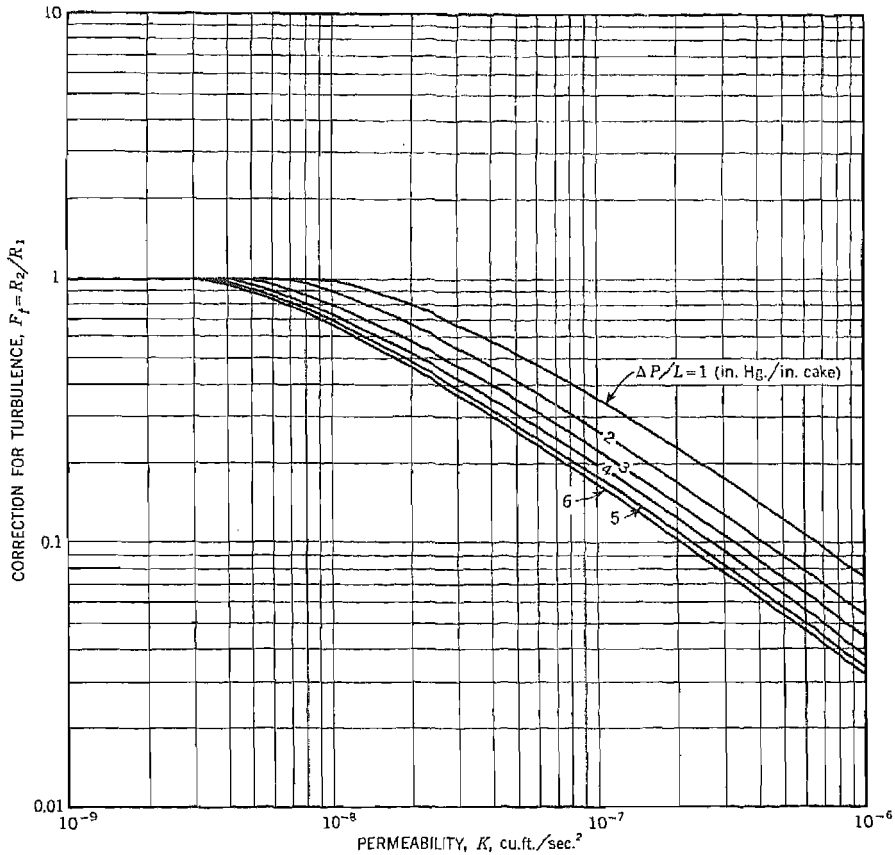


Fig. 3. Correction for turbulence (satd. air at 60°F.) (1).

approaching the residual saturation. Figure 1 shows the decrease of the saturation as a function of the time ratio,  $t/C_t$ , with parameters of residual saturation,  $S_r$ . The filtration constant,  $C_t$ , is defined as follows:

$$C_t = \mu_L XL^2/K(-\Delta P_c) \quad (26)$$

where  $\mu_L$  = the viscosity of the filtrate, lb./ (sec.) (ft.). Figure 1 is based upon equations for laminar flow of the filtrate, integrated with some approximations (1), and permits rapid determination of the curve of moisture content versus time for moisture removal by air flow.

When removing the filtrate by air flow, the quantity of air that must be drawn



through the cake is an important consideration, particularly in vacuum filters, as it determines the required capacity of the vacuum pumps. As the cake is depleted of liquid, the air flow increases from zero to a maximum, the maximum being virtually that obtained with a dry cake. To predict blower requirements, the accumulative air flow must be determined by integration of the instantaneous rates of air flow. Since the air flow usually is in the early transition region between laminar and turbulent flow, relationships have been derived on the basis of laminar flow (see Fig. 2) with a correction factor for turbulence (see Fig. 3) (1). In Figure 2, the accumulative volume of air,  $V_a$ , is shown as a function of time,  $t$ , and filtration constants  $C_a$  and  $C_t$  with parameters of residual saturation,  $S_r$ . The filtration constant  $C_a$  is defined as follows:

$$C_a = XL\mu_L/\mu_a \quad (27)$$

where  $\mu_a$  = viscosity of the air, lb./ (sec.) (ft.). Figure 2 permits a rapid determination of the accumulative air flow for conditions of laminar flow. However, a correction must be made for turbulence. As velocity is the only variable, the correction becomes a ratio of two Reynolds numbers, that calculated by laminar flow relationships, and that on the transition curve. On a Reynolds number friction-factor plot these two Reynolds numbers lie on a line with a slope of  $-2$ , because velocity is the only variable. The plot of the correction factor in terms of permeability,  $K$ , and pressure gradient,  $\Delta P/L$ , is shown in Figure 3. Although the air flow may increase from zero to a maximum during a filter cycle, the Reynolds number for the air remains virtually constant over this range, provided pressure gradient and air properties remain constant. Therefore, a single evaluation of the correction for turbulence is sufficient.

#### WASHING OF FILTER CAKES

Wash water or wash liquor is often used either with air flow or alone to remove the filtrate. During the initial period of washing, the filtrate is removed by displacement.

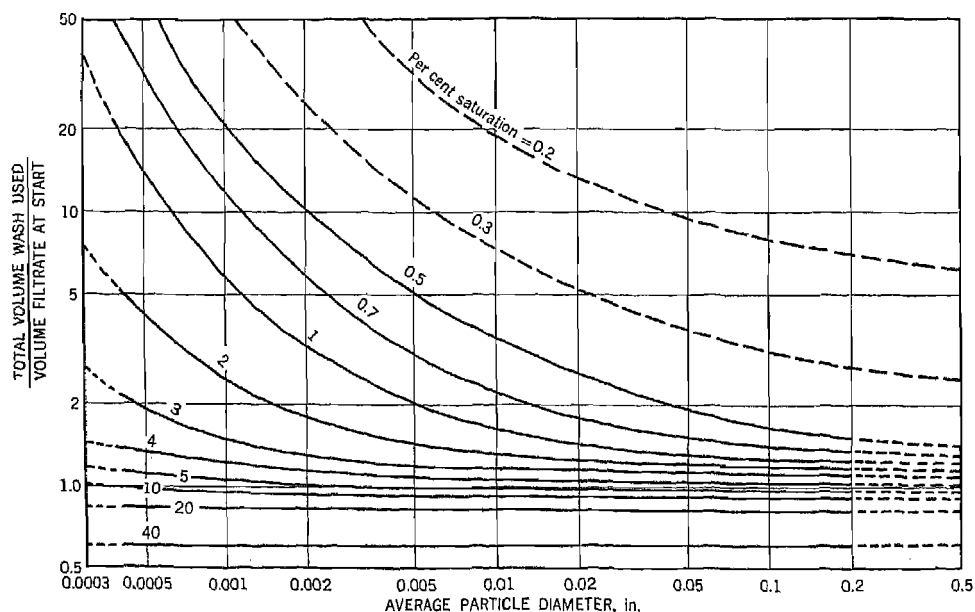


Fig. 4. Washing curves in porous medium.

In washing a filter cake saturated with filtrate, about 90% of the filtrate may be removed undiluted before the interface of wash breaks through the cake. The remaining portion of filtrate is removed with increasing difficulty as washing proceeds, and is limited by the size of the particles in the filter cake. Figure 4 shows the amount of wash required to reduce the filtrate to a given saturation, as a function of the average particle size and the volume of filtrate originally present in the filter cake. In case the viscosity of the wash,  $\mu_w$ , differs from that of the filtrate,  $\mu_f$ , a correction factor,  $\theta$ , is required. Also in the case where the filter cake is less than 100 particle diameters in thickness ( $L/D < 100$ ) a correction factor  $\delta$  is required to account for the ineffective wash resulting from channeling. Figures 5 and 6 show these correction factors. The

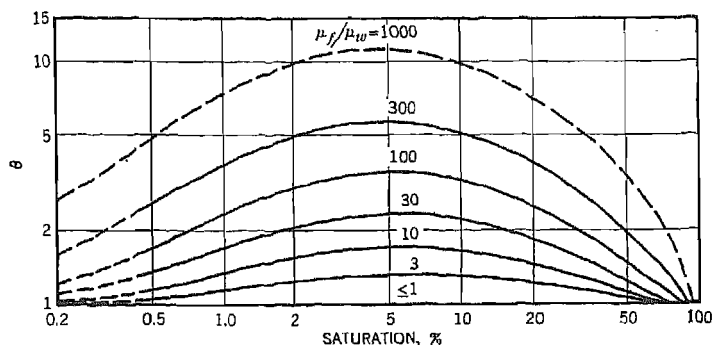


Fig. 5. Correction factor for viscosity ratio.

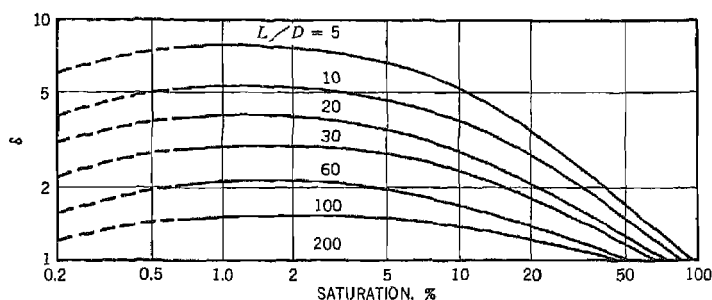


Fig. 6. Correction factor for channeling.

corrected volume of wash is obtained by multiplying the volume of wash determined from Figure 4 by correction factors  $\theta$  and  $\delta$ .

In the case where the wash does not follow the path of the filtrate, as in some filter presses, additional channeling occurs, and the effect of this must be evaluated experimentally. This is also true when an uneven cake is produced or where the wash is applied nonuniformly.

The rate at which the cake will pass wash during air flow is shown in Figure 7. This is a plot of the ratio of the rate of wash with air flow,  $V'_L$ , to the rate of wash without air flow,  $V_L$ , versus the ratio of the rate of air flow during washing,  $V'_a$ , to the rate of air flow through the dry cake,  $V_a$ . The plot shows parameters of residual saturation,  $S_r$ , and cross parameters of saturation,  $S$ . The rates  $V_L$  and  $V_a$  are determined from the Darcy equation (see eq. 1). As a result, selection of the air rate,  $V'_a$ , fixes the washing rate,  $V'_L$ , or vice versa.

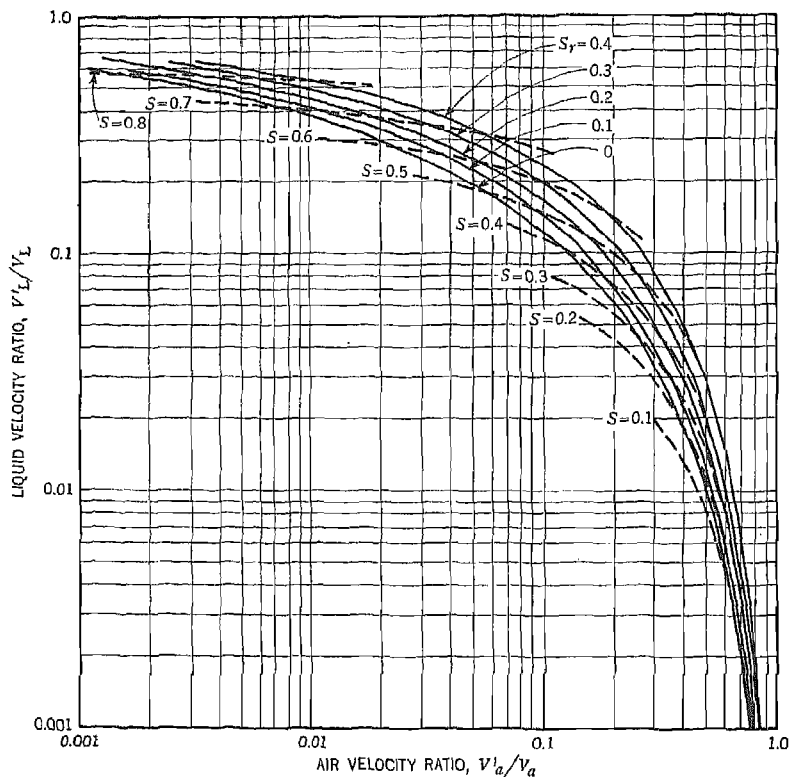


Fig. 7. Washing curves (1).

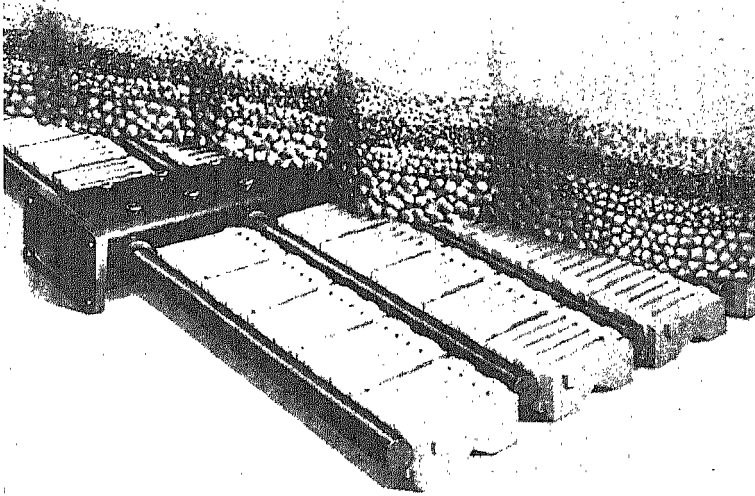
### Filtration Equipment

Filtration equipment may be classified according to the driving force (gravity, pressure, or vacuum), the method of operation (batch or continuous), or whether the filtrate or the cake is the product most desired. (The latter classification is recognized as a generality, as in many cases both the filtrate and cake are desired.) Thus a filter may be designated as a gravity water filter or a continuous vacuum salt filter.

From the standpoint of filtrate capacity, the **batch gravity water filter** is utilized to process more gallons of filtrate than any other type of filter (see *Water, industrial and municipal*). Nearly all city water plants and many industrial plants use this type of equipment. These filters consist of tanks filled with a porous material, usually sand (sometimes anthracite), through which the fluid flows, leaving the tank through a manifold system (underdrain) at the bottom. The sand acts as the filter medium and filters out suspended solids, silt, coagulated hydrated alumina from alum treatment, etc. The filtering sand is supported by a coarse packing such as gravel or crushed rock placed at the perforated bottom. The different sizes of material are laid in layers to avoid mixing particles of different sizes. Each graded size of filter medium should be uniform in particle size so as to achieve maximum porosity and maximum filtering rate.

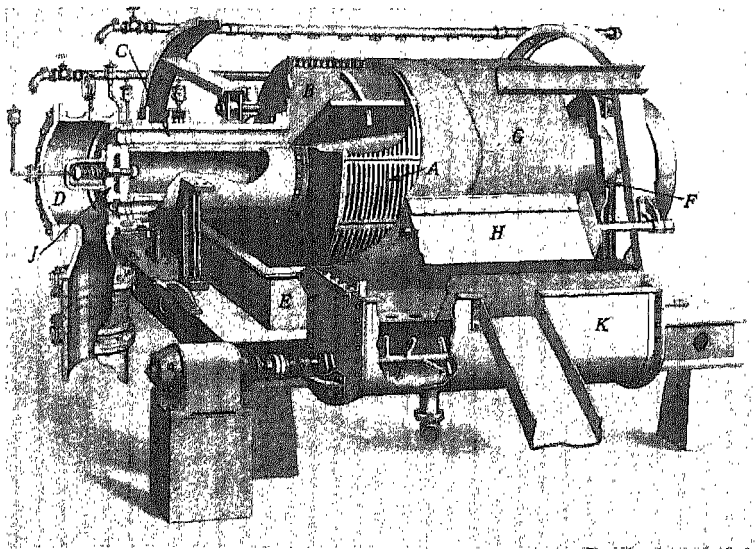
During continuous operation, the pores of the sand in the filter eventually become clogged with the solids removed from the filtrate, necessitating the removal of these solids by backwashing at intervals to maintain or renew the capacity of the filter.

Ducts, equipped with gates or valves, are provided for this purpose. The constant accumulation of solids reduces the average effective capacity to less than half of the calculated value for clean conditions. For continuous plants, a number of filter beds



*Courtesy Infilco Incorporated.*

**Fig. 8.** Section of a gravity sand filter with underdrain manifold system (26).



*Courtesy Whiting Corporation.*

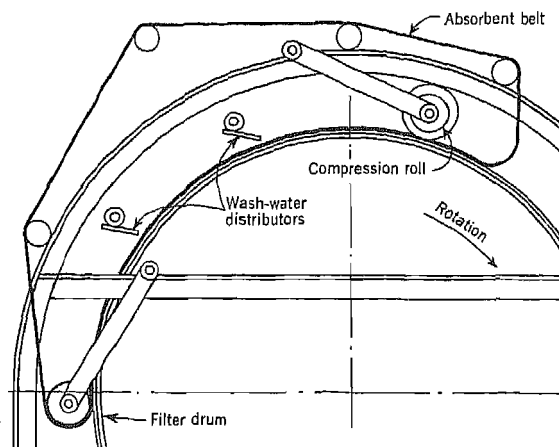
**Fig. 9.** Rotary-drum vacuum filter, salt type (21).

are used, with a schedule of backwashing individual beds in turn. Figure 8 shows a typical section of a gravity sand filter with an underdrain manifold system.

The rates of filtration vary from about 2 gal. per square foot per minute for municipal water purification to about 5 gal. per square foot per minute for some

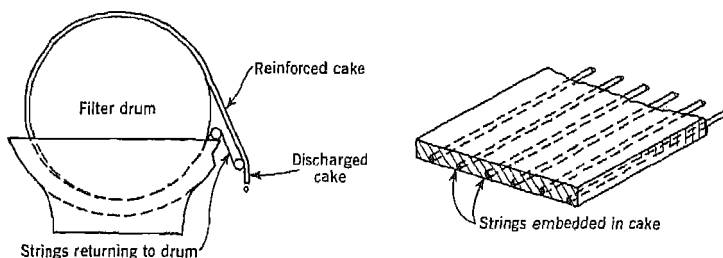
industrial uses. Washing is usually done at a rate of about 15 gal. per square foot per minute. For each particular bed there is a definite velocity at which the wash water will begin to fluidize the bed and release trapped particles. This is the proper washing velocity. For high-capacity service, the filter bed may be placed in a closed vessel and operated under pressure. Smaller sizes are usually enclosed in vertical vessels.

From the standpoint of filter-cake capacity, the **rotary vacuum filter** is the work horse of industrial filtration. The most used filter of this type is the rotary-drum vac-



*Courtesy Filtration Engineers, Inc.*

Fig. 10. Rotary-drum vacuum filter with compression belt and rolls (15).



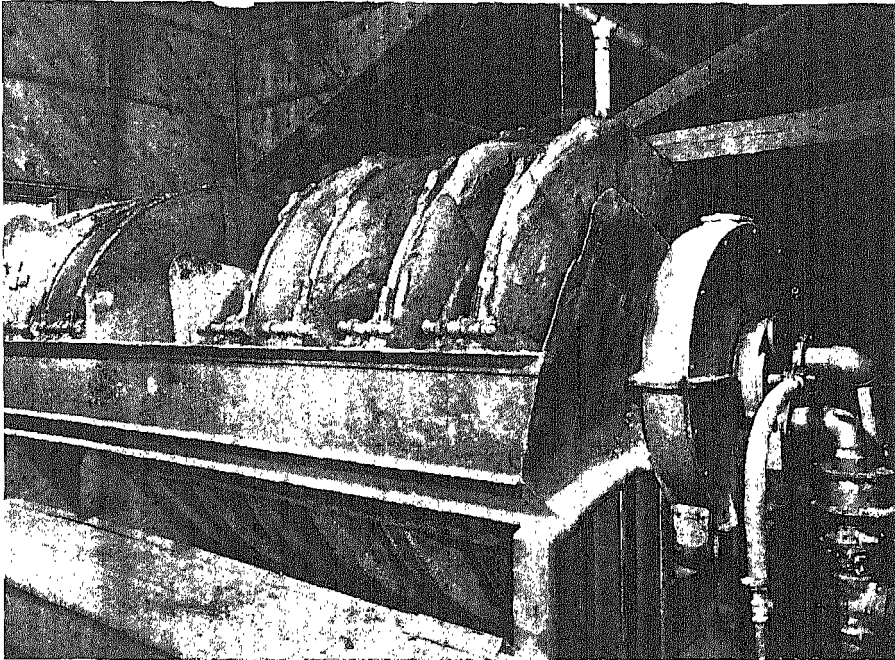
*Courtesy Filtration Engineers, Inc.*

Fig. 11. Rotary-drum vacuum filter with string discharge showing strings embedded in cake (15).

uum filter. After an early period of rapid development at the beginning of the 20th century, the mechanical design of rotary-drum vacuum filters became more or less fixed with but few modifications since that time.

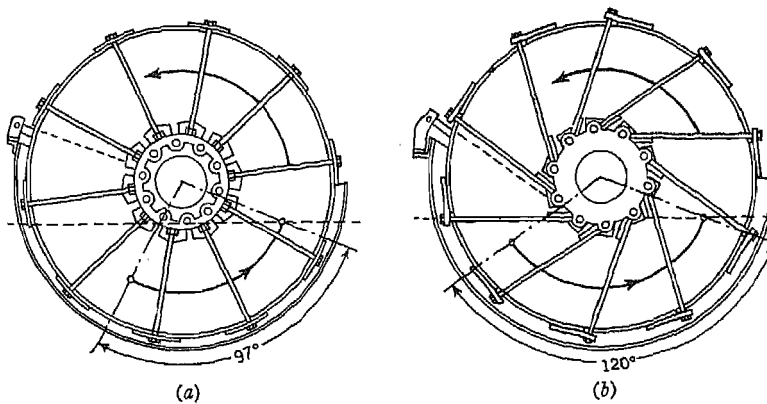
A cut-away view of a *rotary-drum vacuum filter* is shown in Figure 9. The drum, *A*, is divided into sections, *B*, each connected through ports, *C*, in the trunnion to the discharge head, *D*. The slurry is fed to a tank, *E*, in which the solids are held uniformly in suspension by an agitator, *F*. As the drum rotates, the faces of the sections pass successively through the slurry. The vacuum in the sections draws filtrate through the filter medium, *G*, depositing the suspended solids on the filter drum as a cake. As the cake leaves the slurry, it is completely saturated with filtrate and undergoes *dewatering* by the simultaneous flow of air and filtrate. Then the cake may be

sprayed with wash water, after which a second dewatering usually occurs. The filtrate or wash is removed by the combined processes of fluid flow and drying; however, the drying is negligible when using air at room temperature. Finally, the cake is removed



*Courtesy The Eimco Corporation.*

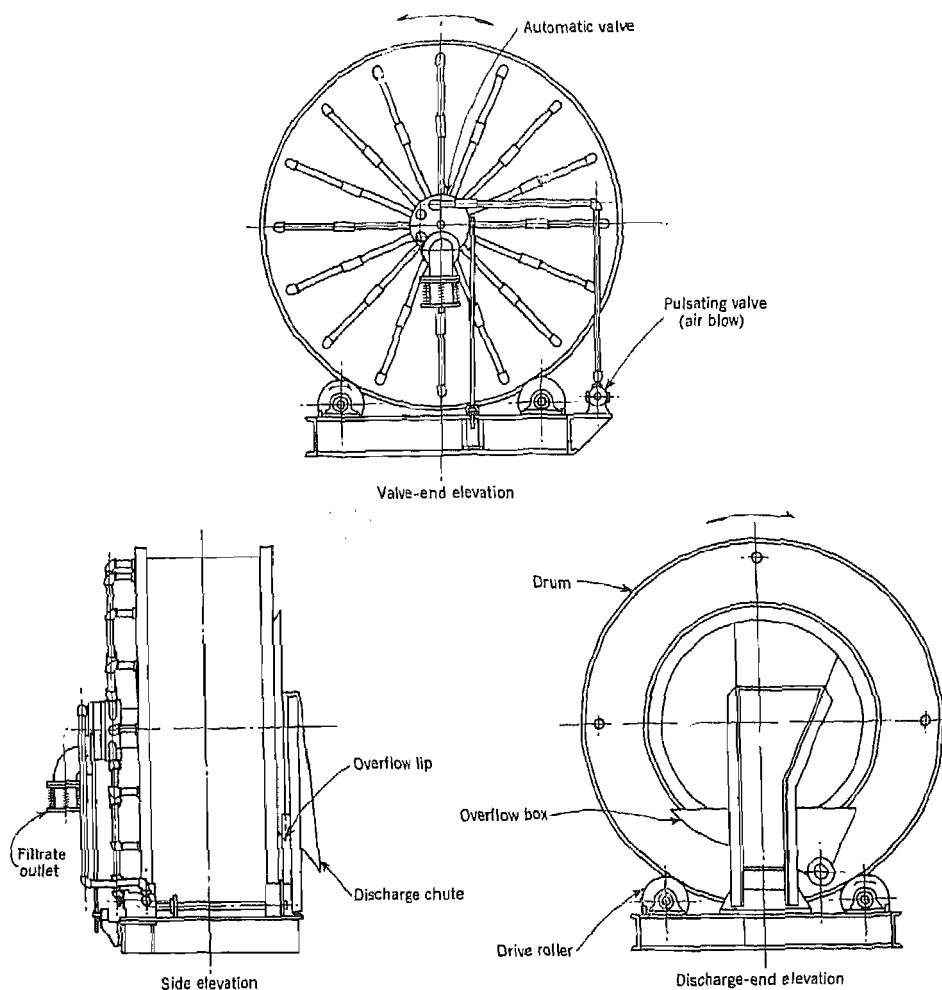
**Fig. 12. Disk-type rotary vacuum filter.**



**Fig. 13. Disk-type rotary vacuum filter showing: (a) pie-shaped sector disk (5); (b) tangential-segment disk (a, courtesy General American Transportation Corporation; b, courtesy Albert L. Genter).**

by a scraper, *H*, which may be assisted by a slight air reversal through the filter valve, *J*. The filtrate and air pass into sections *B*, then through ports *C*, and through discharge head *D* into a receiver, where the air is removed by means of a vacuum pump

and the liquid by a filtrate pump. The dewatered cake may be discharged to a conveyor, or to a repulper, *K*, for repulping with water or weak liquor. Continuous rotary filters of this general type provide high filtering rates, excellent washing, and are available in a wide range of sizes from about 3 to 800 sq.ft. of filter area.



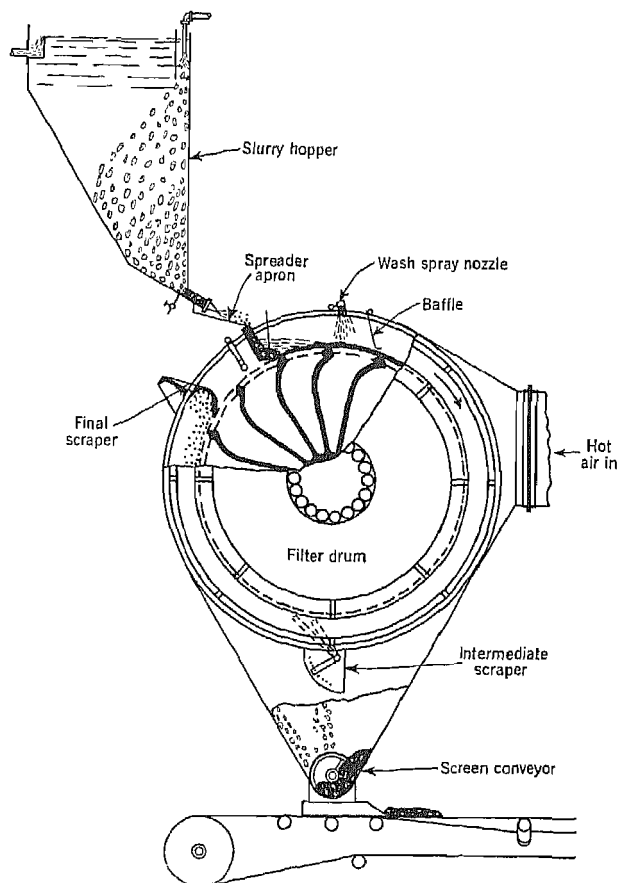
*Courtesy The Dorr Company.*

**Fig. 14. Internal rotary-drum filter.**

Some rotary-drum vacuum filters such as the dewaxing filters used in removing paraffin wax from lubricating oils have no agitators. In the solvent-dewaxing process, volatile solvents such as methyl ethyl ketone and benzene are used to increase the filtering rate and lower the solubility of the wax. The high vapor pressure of these solvents necessitates the enclosure of the filter in a vaportight hood.

The dewatering of cakes composed of fine particles, such as precipitated calcium carbonate, causes shrinkage of the cake with the development of checks and cracks. Unless these cracks in the cakes are closed, large quantities of air will pass through the

openings causing a decrease in vacuum or an increase of the load on the blower. Various attachments may be added to the filter to prevent the development of cracks in the cake. Compression rolls, compression belts, and rubber "spankers" are used to compress the cake sufficiently to prevent development of cracks and to aid in dewatering. Figure 10 shows a compression belt and rolls. In this particular design the wash is allowed to flow through the blanket without atomization, whereas in most filters the wash is sprayed onto the cake by means of a bank of atomizing jets. Flooding the blanket gives uniform wash distribution and decreases the blower requirements.



Courtesy Whiting Corporation.

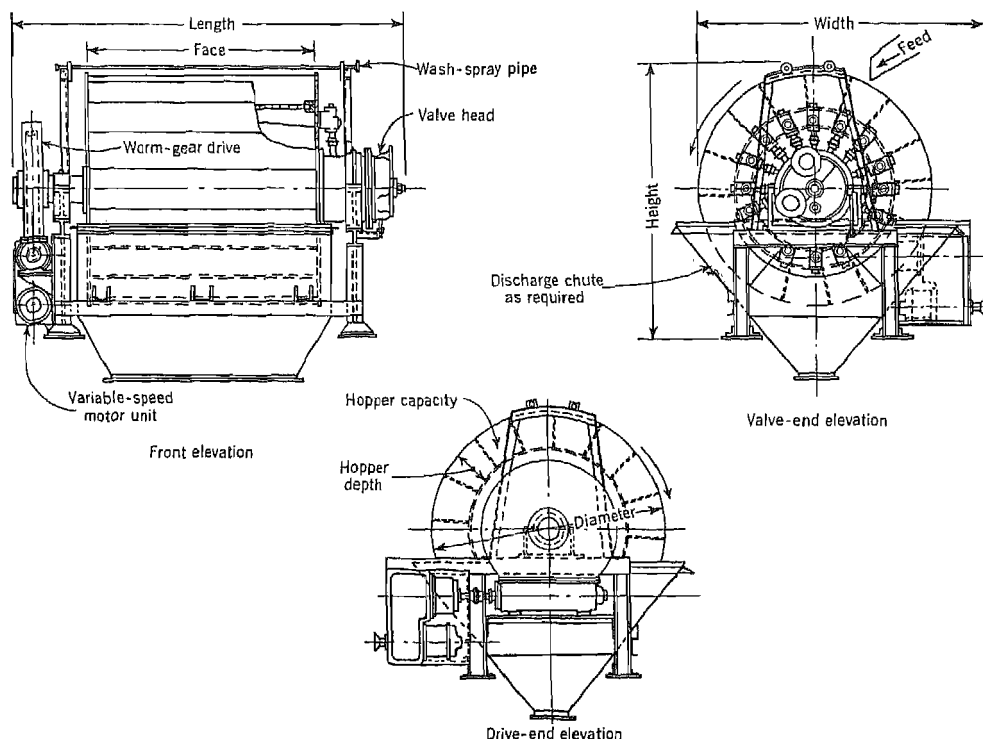
Fig. 15. Top-feed filter (22).

One design of a rotary-drum vacuum filter employs a string discharge in which the cake is removed by a series of individual endless strings passing around the filter and over a discharge roll (see Fig. 11). The strings are usually arranged on  $\frac{1}{2}$ -in. centers. String discharge is particularly effective with fibrous materials such as paper pulp, which forms a cake sufficiently strong to prevent the strings from pulling through the cake as it leaves the drum.

The *disk-type rotary vacuum filter* operates on the same principle as the continuous rotary-drum filter, but has the filter area arranged in disks rather than on the circum-



ference of a drum (see Fig. 12). The individual sectors may be changed independently while the filter is in operation in order to facilitate replacement of the filter medium. These sectors may be pie-shaped or of the tangential-segment type (see Fig. 13). The tangential segment provides a longer period for cake deposition and is used for slurries which filter more slowly. The slurry compartments may be separated for the different disks, by placing one or more division plates in the tank. By this means, two or more products may be filtered simultaneously and separately on the same filter, providing



Courtesy General American Transportation Corporation.

Fig. 16. Rotary-hopper vacuum dewaterer (5).

the filtrates may be mixed. The chief advantage of the disk-type rotary vacuum filter is the greater filtering area it provides, as compared to a drum filter of equal size. However, washing the cake is difficult because of the vertical position of the cake. The cake may slough from the disk and is usually discharged with a higher moisture content than would be obtained with a drum filter. Sizes range from about 22 to 2800 sq.ft. of filter area.

The *internal rotary-drum filter* is of the revolving drum type, but filters on the inside of the periphery as indicated in Figure 14. Because of the relatively short arc of travel between the cake-forming, -washing, and -discharge zones, this type of filter is not satisfactory for slow-filtering slurries or where a thoroughly washed cake is required. It is, however, an ideal filter for use on rapid-settling slurries which do not require a high degree of washing. The difficulty of keeping such slurries in suspension makes the rotary-drum vacuum filter less satisfactory for such material. If the slurry

has particles of different sizes, the cake formed in this filter is properly stratified, with the large particles adjacent to the filter medium.

The *top-feed filter* is illustrated diagrammatically in Figure 15. It is equipped for the use of heated air for drying the solids. The feed is pumped into the hopper, wherein suspended solids tend to settle to the bottom, while excess liquor overflows and may be returned to the process. The slurry or pulp is carried through nozzles by injecting filtrate. The slurry strikes the spreader apron and flows over feed dams. A baffle spreads the slurry on the surface of the drum, followed by formation of the cake and primary dewatering. The cake is then washed by water from the wash spray nozzles. Washing is followed by a second dewatering, which removes the major part of the liquor before the cake enters the drying section. Heated air is blown in through the air duct into the hood surrounding the drum at a positive pressure to prevent the in-leakage of cold air, then through the cake, and out the ports. Drying is followed by removal of the outer crust of the cake by the intermediate scraper. The thinner, partly dried cake continues through the final part of the drying cycle, and is completely removed by the final scraper. Spray from cleaning spray nozzles cleans the filter medium and the cycle is repeated. The dry product drops to the bottom and is picked up by the screw conveyor and discharged onto the belt conveyor.

Top-feed filters are well adapted to handling solids which settle readily and filter quickly, and they have the advantage of producing a dry product. They are not as flexible or as simple to operate as a rotary-drum filter, and should not be used if a turbid filtrate is objectionable.

For slurries containing a small quantity of finely divided material it is desirable to have the coarser materials deposited adjacent to the filter medium, with the finer material on the outside of the cake. Sedimentation in the slurry bed at the top of the filter may be used for this purpose in the top-feed filter and also in the internal rotary-drum filter.

The *rotary-hopper vacuum dewaterer* is a rotary-drum vacuum filter using top feed with radial fins and end walls extending from each compartment to form a series of hoppers, as shown in Figure 16. This filter is particularly suited to handle fast-settling slurries which produce cakes having thicknesses of 4 in. or more. The hoppers prevent the cake from falling from the drum. The high cake thickness combined with relatively high rates of rotation permit this filter to handle very large capacities, in some cases as high as 2000 tons per day of solids with about 6% moisture. These filters are simple to operate, permit flood washing in the hopper, and can produce clear filtrates. Drums are made up to 14 ft. in diameter with a face width of 16 ft.

*Precoat filters*, in which the ordinary filter medium is coated with a porous cake to a thickness of  $1\frac{1}{2}$ –2 in., have been developed for the clarification of liquors containing slimy material or finely divided solids which are difficult to filter (see Fig. 17). The operation consists in building up a porous cake of material, such as diatomite, to the desired thickness in the same manner as would be used for building up any filter cake. The slurry of diatomite is then removed from the pan, and the liquor to be clarified is admitted. The scraper, or doctor knife, is set on a vernier scale to remove a small thickness of the cake at each revolution. In this way extremely thin cakes may be built up and removed almost as quickly as formed, and a high filter rate is maintained. As the knife advances into the cake, which is necessary to insure complete removal of the thin film of solids, the precoat filter medium is finally removed and must be replaced by removing the liquor from the pan and again building up the precoat by using a

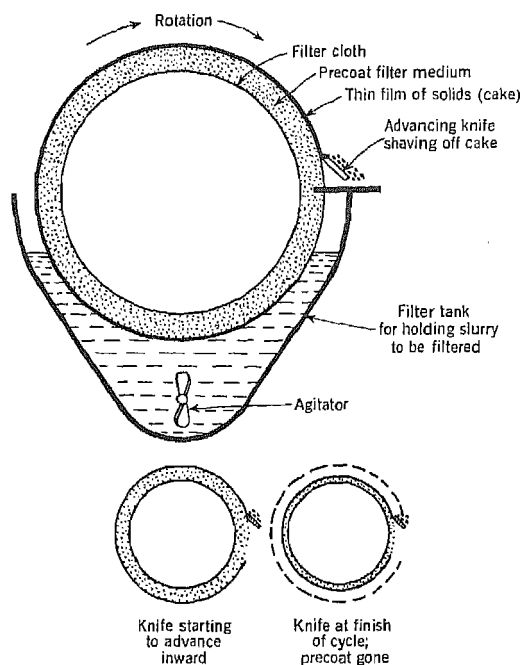
slurry of the precoat material in the pan. Precoating requires approximately two hours, while actual filtration may extend over periods of eight hours or longer.

Precoating is not limited to the particular design described, but may be used on a wide variety of filters, especially with batch filtration. In a batch operation, a thin precoat of  $\frac{1}{8}$  in. or less may be applied before filtering the slurry and the precoat is discharged with the filter cake at the end of the cycle. The addition of some filter aid to the slurry often permits the use of a longer cycle.

The **plate-and-frame filter press** is probably the cheapest per unit of filtering surface and requires the least floor space. The labor cost of opening and dumping

such presses is high, particularly in the large sizes. For this reason they are not used when a large quantity of worthless solid is to be removed from the filtrate. If the solids have high value, and particularly when the quantities to be handled do not justify a continuous filter, the cost of labor per unit value of product may be sufficiently low to indicate the advisability of using a plate-and-frame filter press. It has a high recovery of solids, and the solid in the form of a cake may be readily handled in a tray or shelf dryer, which is frequently used for valuable products.

There is a great variety of filter presses employing plates and frames. The simplest type has a single conduit for introducing slurry and wash water, and a single opening in each plate for removal of the liquid (open delivery), as shown in Figure 18.



Courtesy Oliver United Filters, Inc.

Fig. 17. Operation of a precoat filter.

Other types have separate conduits for introducing the slurry and wash water. Some also have separate conduits for removing filtrate and wash water (closed delivery), illustrated in Figure 19. The conduits may be at the corners, center, or intermediate locations.

The feed slurry enters through the conduit formed by holes in the upper right corner of both the plates and frames. Each frame carries an inlet or hole leading from this conduit to the space between the plates. Pressure on the slurry fed to the press causes the filtrate to pass through the cloths on either side of the plates and run through the space between the cloth and the plate toward the outlet, which may be either a spigot or a second channel formed by holes drilled through another corner of the plates and frames, with outlets provided from the plates but not the frames. The plate is so drilled or constructed that the filtrate enters the outlet from both sides of the plate.

The solids in the slurry accumulate on the cloths on opposite sides of the plates. After due time only a small part of the space between the plates is available for the slurry, and the feed is shut off. If the cake is to be washed, clear washing fluid is then

passed into the inlet, enters the cake from the center of the frame, and passes toward the plates on either side. After the cake has been washed, this flow is stopped, the force holding the plates together is released, the plates and frames are opened in

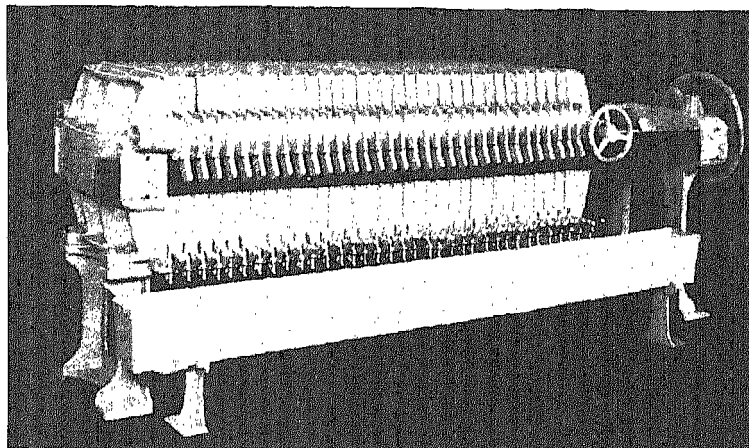


Fig. 18. Plate-and-frame filter press with open delivery.

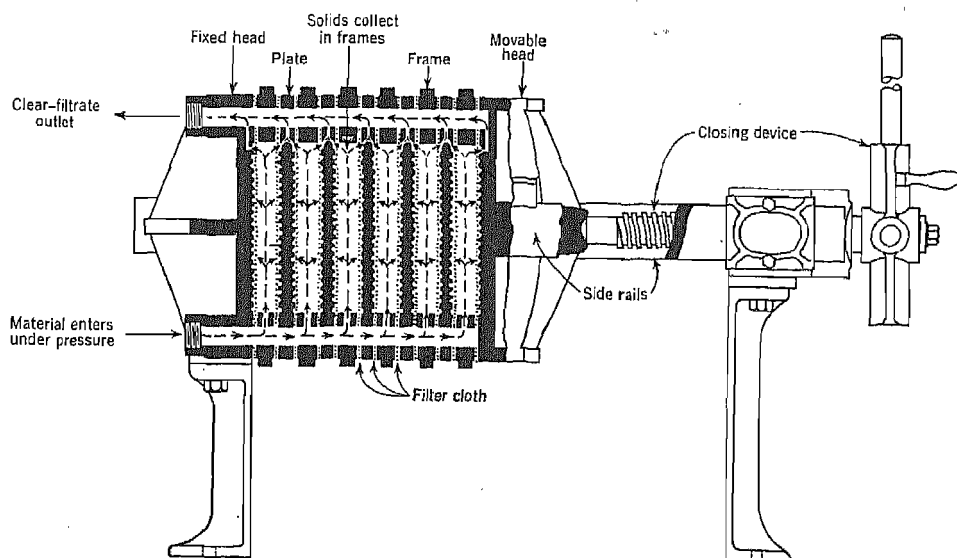


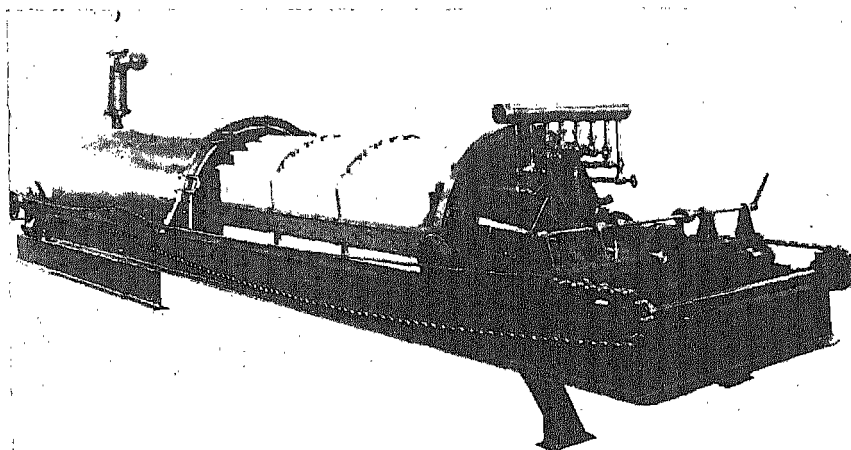
Fig. 19. Plate-and-frame filter press with closed delivery (8a).

sequence, and the cake is removed or dumped into a pit below the press. After dumping is completed, the press is again closed by applying the mechanical force to lock the plates and frames together, and a new cycle of filtration begins.

**Batch leaf filters** (see Fig. 20) are similar to the plate-and-frame filter in that a cake is deposited on each side of the leaf and the filtrate flows to the outlet in the

channels provided by the coarse drainage screen in the leaf between the cakes. Flow of the slurry may be caused by either pressure or vacuum. The leaves are immersed in the slurry and the cake is allowed to build up on both sides of the leaf until the desired thickness is formed, or until the filtration rate drops off sharply. The leaves are held in a vertical position. For pressure filtration the leaves are circular in shape if aligned perpendicular to the axis of the cylindrical tank in which they are enclosed. Rectangular leaves are aligned parallel to the axis of the tank.

Leaf filters for vacuum filtration may be constructed of a large size in which the leaves are suspended on a crane and introduced into a pit containing the slurry. After the cake has been built up to the desired thickness, the crane lifts the leaves and cake out of the pit containing the slurry and immerses the leaves in a second pit containing the wash solution. A vacuum is held on the filtrate or wash side during filtration, transfer, and washing. After the cake has been adequately washed it is similarly



*Courtesy Oliver United Filters, Inc.*

**Fig. 20. Batch leaf filter.**

transported to a third pit for dumping before the clean leaves are returned to the slurry pit for filtration.

Stationary-leaf filters sometimes tend to produce a pearshaped cake because of the settling of solids in the slurry. This may be corrected by using a rotary-leaf pressure filter. In this design, a battery of circular leaves rotates about a central hollow shaft which also serves to remove the filtrate. The rotation of the leaves produces a uniform cake and permits uniform washing and dewatering with compressed air. Reversal of the compressed air causes the cake to fall from the leaves to a screw conveyor below, which removes the cake from the filter without the necessity of opening the filter.

#### SPECIAL INDUSTRIAL FILTERS AND LABORATORY FILTERS

The equipment that has been described so far is of the type used in large-scale chemical processes and similar operations. However, a great number of filters of special design are used in other industries.

*Clarifying pressure filters* such as the "filtermasse" filter are used extensively in the beverage industry to "polish" the beverage, that is, to produce a brilliantly clear

filtrate. In the filtermasse filter, the turbid liquid passes through a bed of porous fibrous material such as cotton fibers, glass wool, or fluffed wood pulp. The filter beds are usually  $\frac{1}{2}$ –2 in. thick and may be in the shape of flat disks or cylinders. Large-size disks may be 24 in. in diameter with 40–60 disks in series. Such filters may be used to remove dead yeast cells from beer to produce a brilliant beverage. Smaller sizes in various modifications have been used as oil filters on automobile engines, fuel-oil lines, and similar installations. One special design of clarification filter suitable for acids and corrosive fluids has a porous ceramic tube as the filtering element.

*Edge filters* consist of a series of annular disks stacked in a cylinder with close clearances between disks and forming a hollow tubular passage through the center. The cylindrical stack of disks is enclosed in a cylindrical cartridge or vessel. In operation the fluid enters the cartridge between the wall and the disks, passes from outside the disks through the clearances between the disks, and discharges through the central tube. The outer edges of the disks act as the filter medium. The clearances between the disks control the size of particle that the filter will pass. A filter cake eventually builds up on the outside of the disks. This cake can be discharged by reversing the flow of fluid. In some designs, cleaner blades are placed in the clearances between the disks, and a simple rotation of the cartridge cleans the disks. This type of filter is often used to remove dirt from industrial fuel oil.

*Bag filters* operate like the bag on the household vacuum cleaner and are used to remove dust and fine particles from an air stream. Usually a number of cloth bags are operated in parallel. Agitation of the bags at intervals causes the solids to fall to the bottom of the bag, where they accumulate until the bag is emptied. These filters are frequently used to recover the fine particles formed in a screening or crushing operation. In such an installation a blower removes the dust-laden air from the screening or crushing equipment and carries it through ducts to the bag filters. If large quantities of dust are involved a cyclone separator (see *Gas cleaning*) may precede the bag filters. Electrical precipitation may also be used (see *Electrostatic precipitation*). When small amounts of dust are to be filtered from air streams, the air may be passed through glass-wool filter frames. The glass-wool bed is usually 1–2 in. thick, is very porous, and is supported on wire screens. Treating the glass wool with an oil aids in retaining the dust. Such filter frames are commonly used in household-heating plants using hot air with forced circulation.

Many other industrial filters of special design exist. A large number of presses such as cider presses and oil-cake presses have a combined function of pressing and filtering. Filters used in the manufacture of fine chemicals are often large-sized or modified laboratory filters.

Most laboratory filters are vacuum filters. The simplest type is the glass funnel using a piece of filter paper folded to form a cone. The Büchner laboratory filter gives more positive filtration and contains a perforated false bottom which is covered with a circular piece of filter paper. The Gooch laboratory filter is a porcelain or platinum crucible with a perforated bottom. A precoat of specially prepared asbestos fibers acts as the filter medium. Bacteriological candle filters, microfilters, etc. are used for particular laboratory techniques.

#### FILTER MEDIUMS

The filter medium is the essential part of a filter which retains the suspended solids but permits the flow of the fluid. In general, filter mediums may be divided into

two groups: *en masse* mediums in which the medium is the primary filtering agent throughout filtration, as in the case of the sand in the sand filter; and initiating mediums in which a thin cloth or screen starts the formation of a filter cake which then becomes the filter medium. *En masse* filter mediums may be classified into two groups: crystalline or granular mediums that are cleansed by backwashing for re-use; and fibrous "filtermasse" mediums that must be replaced after collecting a quantity of solids (some may be re-used after a special wash treatment). Initiating mediums may be divided into metallic and nonmetallic screens or cloths.

Sand is the most widely used *en masse* granular filter medium, largely because of its availability, stability, and low initial cost. The sand forms a labyrinth path for the turbid fluid. Although a suspended particle may penetrate some distance into the bed by passing along the large channels, the particle will eventually be entrapped in one of the smaller interstices, if the bed is of sufficient depth. A filter bed of fine sand may be replaced by a deeper bed of coarser sand to give the same filtration. The coarser sand will have the greater filter capacity because of its greater permeability. In practice, sand filter beds of 2 ft. or more are common with an additional foot or more of supporting graded sand. Filter-sand particle sizes of 30–40 mesh are common. It is important that the sand be of uniform size to obtain maximum porosity; also care must be used not to mix the coarser supporting sand and gravel with the filter sand, since this decreases the porosity. Anthracite coal fines are also used as a granular medium. Since the coal has only about half the bulk density of sand, it is much easier to fluidize the bed during backwashing. Coal particles have smooth surfaces and are easily washed.

The principal fibrous *en masse* filter mediums are cotton fibers and fluffed wood pulp, although glass wool is used in some cases. In the smaller units, the disks or cartridges are usually single-service units, and inexpensive materials such as cotton and wood pulp are economical to use. The small size of the fibers makes it possible to clarify a fluid in a relatively thin bed of 1 or 2 in. in thickness. Fibrous materials produce beds of high porosity (90–95%), and this tends to compensate for the small particle size. Sand of a comparable particle size has a porosity of only about 40% and, therefore, has a much lower permeability than the corresponding fibrous medium. For this reason, extremely fine sand is seldom used in commercial filtration. Diatomite (*q.v.*), when used as a precoat, acts as a granular filter medium. It has a porosity of about 80%.

Most continuous filters use woven-mesh metallic initiating filter mediums. Such filter mediums can be made of any metal that can be wire-drawn, for example, steel, stainless steel, special alloy steel, copper, bronze, nickel, Monel, silver, and lead. In the case of lead construction, perforated sheet lead is used because of the weakness of lead wire. Corrosion resistance is usually the controlling factor in the selection of the metal. Monel is widely used for various aqueous solutions. The selection of mesh is usually controlled by the largest particle size in the slurry being filtered. The opening should be larger than the particle, so as to prevent the particle from lodging in the opening and blinding the filter. Metallic filter cloths are available in plain and twill weaves and in corduroy twilled or stranded weaves. In specifying the mesh, mesh size usually refers to the number of wires per linear inch in either direction, the warp (running the length of the cloth) being given first.

Cotton is the most widely used nonmetallic initiating filter medium. It is used extensively in filter presses and on continuous filters handling slurries with particles of

fine size. The cotton usually is used in the form of a woven fabric such as duck or twill. Cotton flannel formerly was used extensively in the milk industry for dirt removal; however, unwoven cotton fiber disks for single-service use have replaced flannel in many instances. Different weaves have different filter characteristics and no general rule applies. Table I gives some general characteristics (7).

TABLE I. Filtering Characteristics of Cotton Fabrics.

Weave	Tensile strength	Clarity of filtrate	Rate of flow	Cake discharge	Freedom from blinding	Shrinkage
Canton flannel.....	Fair	High	Fair	Poor	Good	Even
Chain.....	Low	High	High	Fair	Fair	Uneven
Duck.....	High	Fair	Poor	Good	Poor	Even
Muslin.....	Low	Poor	High	Good	Good	Even
Twill.....	Fair	Fair	High	Fair	Fair	Uneven

Source: reference (7).

Cotton duck possesses the desirable property of high strength, which tends to give it longer life on the filter than other weaves. However, because of the dense weave it has the lowest filtering rate of any weave listed. A high rate of flow and a clear filtrate can be obtained with a chain weave; however, besides having a low strength, the chain weave tends to shrink unevenly which may cause trouble on drum filters. Some compromise is usually necessary in selecting the weave of the cloth.

Wool may be used for acid solutions (up to 6%) with about the same expected life as in the case of cotton and neutral liquors. Wool cloths are sold on a weight basis, and a weight of 12 oz. per square yard is typical for wool filter cloth. Wool does not give as clear a filtrate as cotton and costs considerably more, which limits its use. It is used for dewatering of sewage sludge.

The new synthetics are finding wide use. Nylon is recommended for rotary filters. It has an unusually high strength even at elevated temperatures. It resists most alkalis and organic acids and common organic solvents such as benzene, carbon disulfide, and chlorinated hydrocarbons. It is not recommended for strong mineral acids and oxidizing agents. Orlon is a new high-strength synthetic which, although not quite as strong as nylon, will give good resistance to strong mineral acids. It also withstands common solvents, oils, and greases, and has fair resistance to weak alkalis. It retains its strength at elevated temperatures. Vinyon N is another improved synthetic that is highly resistant to nearly all acids, alkalis, and most solvents. It resists concentrated hydrochloric acid, concentrated phosphoric acid, and concentrated sodium hydroxide, and is good for hot acids.

Glass filter mediums are woven from glass yarns to produce cloths of similar texture and weave. This filter medium is one of the most stable and inert forms developed (except to strong alkalis). It has high strength, gives high rates of flow, and is easily handled. However, it has some disadvantages. Plate-and-frame presses tend to crush the fibers and the cloth shows low resistance to abrasion.

Rubber filter mediums are available in sheets having pore diameters of 0.004–0.012 in. and containing 1100–6400 holes per square inch. It is claimed that the smooth surface of the rubber mediums permits removal of a thinner cake than with woven fabrics.

Linen and silk are not widely used as filter mediums.



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**FIREBRICKS.** See *Refractories*.**FIRE CLAYS.** See *Clays (ceramic)*; *Refractories*.

## FIRE PREVENTION AND EXTINCTION

Prevention of loss of life or personal injury by fire is the primary objective of fire prevention and extinguishment or control of its spread. The secondary objective is the protection of property. During recent years, fires have caused approximately 11,000 fatalities and between \$650,000,000 and \$750,000,000 property damage annually. In addition, fires have caused a large number of personal injuries and tremendous losses due to interruption of production, destruction of irreplaceable records and materials, and other losses that cannot be measured in dollars.

Although losses have been increasing in recent years, the proportion in relation to the total amount of combustible property has been decreased through measures of fire prevention and extinction. Application of these measures to the chemical industry is based upon a knowledge of the common fire hazards, familiarity with the fire-hazardous properties of the materials being processed or stored, recognition of the principles of fire-safe building construction, and appreciation of the uses and limitations of the various types of fire-protection equipment. See also *Industrial hygiene; Safety*.

In general, to have fire there must be present a combustible material, oxygen or other oxidizing agent, and a sufficiently high temperature to maintain combustion. By removal of the combustible material, elimination or reduction of the oxygen supply, or the cooling of the combustible material below its ignition temperature, fire can be extinguished.

### Common Fire Hazards

**Matches and Smoking.** Careless use of matches and smoking materials is the most prevalent cause of fires and, because of the universality of smoking, is difficult to control. It is generally agreed that the matches used in connection with smoking present a greater hazard than the smoking material itself. The match hazard can be mitigated by the use of safety matches which strike only on the box, but the only sure way to prevent fires from careless smoking is to prohibit smoking in all areas where match flames or the careless disposal of smoking materials may be a serious hazard. Due to the difficulty of enforcing complete prohibition, it will be better to permit smoking in safe locations and at specified times.

**Rubbish.** Although not a cause of fire except when susceptible to spontaneous ignition, rubbish furnishes material for start or spread of fire when permitted to accumulate. Prompt and regular disposal in metal, covered receptacles is essential. Where waste materials are not removed from buildings, they should be kept in fire-resistive vaults and preferably baled. It is also important not to allow rubbish to accumulate outside the plant where it can spread fire. This recommendation also applies to dry weeds and grass, which can be effectively and safely removed by the use of calcium chloride or agricultural borax.

**Cleaning compounds** containing flammable liquids or oils subject to spontaneous heating should be stored and used with regard to their fire-hazard properties. Floor oils containing low-flash-point solvents are a hazard when freshly applied and those containing oils subject to spontaneous heating are hazardous, particularly when left on mops or rags. Used in excess, they increase the combustibility of the floor. The use of sawdust to absorb oils increases the fire hazard. Noncombustible oil-absorptive materials are available.

**Lockers and cupboards** present a fire hazard when used for storage of waste ma-

terials. Regular inspection is necessary to make certain that proper conditions of cleanliness are maintained. The ideal lockers and cupboards are made entirely of steel.

**Cotton waste** is mildly hazardous because it is readily flammable when not baled. Large supplies should be kept in covered metal bins and small supplies, in waste cans, properly marked. Oily waste is particularly hazardous, especially if the oil is susceptible to spontaneous heating. Covered metal cans should be used and emptied daily.

**Packing Material.** Excelsior, straw, sawdust, and burlaps are all hazardous and should be treated as clean waste. Special vaults or storerooms are often required for large quantities.

**Locomotive Sparks.** Sparks from locomotive stacks or coals from ash pans have been common causes of fire. Elimination of combustible roofing, protection of windows with permanent screens, prohibition of locomotives from combustible buildings, and good housekeeping practices for areas outside buildings are remedies for this hazard.

**Friction.** Overheated bearings of the sleeve type are a frequent cause of fire. Shafting well hung and maintained, hangers and bearings kept clear of woodwork, use of self-oiling bearings, and periodic maintenance will minimize the possibility of fire caused by friction. Slipping pulleys and rope drives are also a cause of fires. The hazard is lessened by the use of metal pulleys and canvas belts.

**Mechanical sparks** consisting of small pieces of metal heated by impact or friction can start fires, under favorable conditions, in dusts, cotton, certain highly flammable liquids such as carbon disulfide, and other readily ignitable materials. Leather-faced, plastic, wooden, and certain nonferrous tools are free from this hazard. Magnetic separators minimize the hazard at mechanical equipment.

**Open-flame devices** for heating and lighting possess an obvious hazard in locations containing flammable liquids, explosive dusts, or other readily ignitable material. Electric devices approved for use in hazardous locations are safe substitutes.

**Heating appliances** introduce fire hazards if not properly installed and operated. Required clearances should be maintained between all units and combustible walls and materials. Adequate clearances, safe mountings, and recommendations for safe storage of fuel, installation of chimneys and smoke pipes are set forth in reference (16).

**Electric wiring and equipment** may introduce both fire- and personal-injury hazards. Electricity may become a fire hazard through arcing, sparking, or overheating. The casualty hazard is introduced through burns, shocks, or falls due to shocks. Only suitable and safe materials should be used, and equipment should be installed in accordance with the *National Electrical Code* (15) and the *National Electrical Safety Code* (10).

**Static electricity** may be a hazard wherever flammable vapors, gases, or finely divided combustible materials are present. Although the generation of static electricity cannot be prevented, formation of static sparks can be avoided by preventing the accumulation of static charges. Grounding of surfaces on which static may accumulate, artificial humidification in areas where the hazard of static electricity is present, and ionization of the air are three methods used, singly or in combination, to prevent static charge accumulation.

**Lightning** is a frequent cause of fires in certain geographical locations. To protect a structure against lightning, a properly installed metallic path provided from the highest part of the structure to the ground will carry lightning discharge harmlessly to earth (4).

### Hazardous Materials

**Flammable liquids** have been responsible for many serious fires and explosions in the chemical industry because of improper handling and storage. Flammable liquids, of course, are not themselves the cause of fire but are often referred to as such because ignition sources, which would ordinarily be nonhazardous, may cause serious fires in the presence of flammable liquids. The *Suggested Ordinance Regulating the Use, Handling, Storage and Sale of Flammable Liquids and the Products Thereof* (18) is the generally accepted standard of minimum fire-safety requirements for the storage and handling of flammable liquids. The Interstate Commerce Commission has published regulations for shipping hazardous materials (6).

Several properties of a flammable liquid influence the degree of fire hazard. The flash point, ignition temperature, and explosive limits are of particular importance. The *flash point* of a liquid is the temperature at which it gives off vapor sufficient to form an ignitable mixture with the air near the surface of the liquid or within the vessel used. The *ignition temperature* of a vapor is the minimum temperature required to initiate or cause self-sustained combustion independently of the heating or heated element. The *explosive or flammable limits* are the minimum and maximum concentrations of vapor in air that will propagate flame. A comprehensive list of the more commonly found flammable liquids with data on flash points, ignition temperature, explosive limits, and other properties has been compiled and published (11).

Since it is the vapor of a flammable liquid rather than the liquid itself that burns or explodes, there is no hazard when evaporation cannot take place. All equipment in which flammable liquids are handled and from which flammable liquids may escape should be designed and constructed so as to be as tight as possible. Piping must be inspected regularly for leakage, and storage and manufacturing areas should be tested with a combustible-vapor indicator. Portable safety cans, substantially constructed to minimize the danger of leakage and spillage, are available for handling small quantities of flammable liquids inside buildings. Wherever flammable liquids are handled or stored, it is essential to eliminate all sources of ignition. Smoking should not be permitted and all open-flame or spark-producing devices should be excluded from the areas. Electric equipment should be of nonsparking types and precautions should be taken against static discharge.

Ventilation is necessary to prevent flammable vapor concentrations from reaching the lower explosive limit. Although natural ventilation has the advantage of not being dependent upon manual starting or a power supply, it is less positive than mechanical ventilation. It is standard practice to provide means for venting explosions in rooms and buildings where there is possibility of accumulation of flammable vapors. Large areas of glass and light wall and roof construction are common means of relieving explosion pressure without causing major structural damage. Where flammable liquids are to be handled, the walls should not support the roof, and all piping and other containers of the liquid should be independently supported on the columns and other framing so that should an explosion occur there will be no increase in the resulting fire intensity due to breakage of the containers when the roof or walls fail because of the explosion pressure. These provisions apply as well where combustible dusts or gases are handled.

**Gases.** The hazards of flammable gases are generally similar to those of flammable liquids, and many of the precautions recommended for flammable liquids apply

also to gases. The first requirement for the storage and handling of any gas is a substantial storage container and piping system, free from leaks, strong enough to withstand any pressures to which they may be subjected, and located or protected to minimize the danger of mechanical injury. Since the pressure of a gas in a closed container increases when the gas is heated, storage cylinders and other containers are provided with some form of pressure relief to prevent explosion or rupture in case the container is exposed to fire. Pressure relief is commonly provided by rupture disks, fusible plugs, or safety relief valves.

**Hazardous Chemicals.** The hazardous properties of explosives are recognized and respected; consequently, accidental fires and explosions involving explosives rarely occur. There are many other chemicals that may involve a serious fire and explosion hazard when stored or used without proper safeguards. See also *Explosives*.

To evaluate the fire hazard of a chemical during storage, it is of primary importance to know if the chemical heats spontaneously, reacts with water, explodes on heating, gives off hazardous decomposition products, or reacts dangerously with other chemicals stored nearby. To evaluate its hazards during reaction, it should also be known if the chemical is to be subjected to high temperatures or pressures.

A *Table of Common Hazardous Chemicals* prepared by committees of the American Chemical Society and the National Fire Protection Association contains a list of 98 of those chemicals most frequently met in industry (11). Life and fire hazards, usual shipping containers, fire-safe storage, and fire fighting recommendations are indicated for each chemical. The following general information on certain classes of chemicals commonly met in the chemical industry supplements data on specific chemicals in the table.

**Nitrates.** Inorganic nitrates are noncombustible but have certain properties that promote combustion in other materials. The oxygen evolved when nitrates are heated increases the intensity of any fire in their vicinity. Water solubility is another property that has been indirectly responsible for many serious fires. Bags in which nitrates have been shipped may have become saturated. On drying they will contain an impregnation of nitrate and be highly flammable. It is therefore good practice to transfer nitrates from combustible containers to noncombustible bins and thoroughly wash empty bags and barrels. Large volumes of water are recommended for fire fighting. Carbon dioxide and other smothering-type agents are of little value, and steam is of no value. Ammonium nitrate may be detonated by heating to high temperatures in a confined space or under pressure. See *Ammonium compounds*; *Explosives*.

**Nitrites.** Mixtures of nitrites with combustible substances are hazardous and should not be subjected to heat or flame. Ammonium nitrite and certain others are explosive. Requirements for storage and handling of nitrites and fire-fighting recommendations are the same as for nitrates.

**Metals.** Since nearly all metals will burn under certain conditions, the fire-hazard properties of individual metals being processed or stored should be considered.

The hazard of magnesium and its alloys depends to a large extent upon the size of the individual pieces. Castings are not readily subject to ignition but chips, shavings, and dust are readily ignited. Because of the reaction of magnesium with oxygen, magnesium fire protection presents special problems. Common extinguishing methods depending on water, water solutions, and inert gas are not effective on magnesium fires except where water is applied in sufficient volume to cool the magnesium to below its ignition temperature. Carbon tetrachloride reacts violently with magnesium. Dry

sand, powdered asbestos, and various special powders can be used to extinguish small fires. When large amounts of cast magnesium are involved, however, the best method is to apply large quantities of water from a safe distance. Automatic sprinklers ordinarily will not discharge water at a rate sufficient to extinguish large magnesium fires but will serve to localize the fire.

Because it is far easier to prevent magnesium fires than to extinguish them, fire-prevention measures should be closely followed. Melting units should be kept free of moisture, metal should be dried before being added to the melting unit, and an atmosphere of sulfur dioxide should be maintained above the molten metal. It is good practice to purge molds with sulfur dioxide before pouring and to maintain a sulfur dioxide atmosphere in heat-treating ovens. Dust produced in buffing and polishing operations must be collected with due regard to the explosion hazard. Sharp tools are necessary in machining operations to prevent overheating, and cooling fluids should be of the oil type. Waste magnesium should be placed in covered metal drums and the drums emptied periodically. Loose storage of scrap in bins or burlap bags should not be permitted except in noncombustible buildings.

Aluminum has a sufficiently high ignition temperature so that its burning is not ordinarily a factor in fire, except that fine chips and shavings are subject to somewhat the same sort of combustion as magnesium. Aluminum powder is explosive.

Because of the activity of sodium, potassium, and lithium, special methods of handling are required, and storage should be in a cool location, well separated from oxidizing materials. The common extinguishing agents, such as water, foam, and carbon tetrachloride, should never be used. Special chemical compounds, dry sand, and dry soda ash are effective. These must be kept in closed containers. Sand is effective only on small quantities of burning metal and must be absolutely dry. Soda ash containing over 3% moisture will react with the burning metal.

Iron and steel in their usual massive form do not ordinarily burn but in the form of fine wool or dust may be ignited. Contamination with oil or certain other materials facilitates combustion.

*Nonmetals.* With few exceptions nonmetals are combustible. Hazards of some of the more common members of the group are indicated here.

Lampblack, formed by incomplete combustion of petroleum, often heats spontaneously when freshly bagged. It has great affinity for liquids and heats spontaneously in contact with drying oils. It should be thoroughly cooled before bagging, and stored in a cool, dry place away from oxidizing materials. Lampblack dust can be exploded.

White phosphorus is hazardous because of its ready oxidation and spontaneous ignition in air. It is customarily shipped and stored under water to obviate this danger. Large volumes of water are recommended for fire control, care being taken by fire fighters to avoid the dense white clouds of poisonous fumes evolved. Red phosphorus does not oxidize and burn spontaneously at ordinary temperatures and is not poisonous in the solid form; but when once vaporized, it takes on the fire and toxicity hazards of white phosphorus.

Sulfur is flammable, igniting at 450°F. It melts and flows when burning and evolves large quantities of irritating and suffocating sulfur dioxide. Sulfur vapor forms explosive mixtures with air, and finely divided dust in air can be exploded. Water spray is recommended for fire fighting. Sulfur should be stored away from such oxidizing materials as chlorates, perchlorates, chromates, and nitrates.

*Halogens.* The halogens are noncombustible but will support combustion of certain substances. Turpentine, phosphorus, and finely divided metals ignite spontaneously in the presence of the halogens. Chlorine may react spontaneously to produce fire with ammonia, ethylene, hydrogen, etc. Fluorine may be handled safely in nickel or Monel cylinders, although moisture or other impurities within the cylinder may cause a violent reaction that will melt and ignite the metal. Fluorine cylinders should be stored in a fire-resistive, well-ventilated, segregated room.

*Metal hydrides* will ignite explosively on contact with water. Exposure to air for prolonged periods with absorption of moisture may cause spontaneous ignition, necessitating storage in hermetically sealed containers in a cool dry place. Dry soda ash or other inert smothering material can be used to smother fires involving hydrides.

*Inorganic acids* are not flammable but may cause fire or explosion on mixture with combustible materials. In general, strong acids should be stored in cool, well-ventilated places, away from the sun, and segregated. Water in spray form is recommended for fighting fires in acid-storage areas.

*Nitric acid* or its vapor may materially increase the flammability of wood, and mixtures of organic material and concentrated acid will heat spontaneously. *Hydrochloric acid* reacts with certain metals to liberate hydrogen gas. *Sulfuric acid* causes organic material to char and if sufficient heat is evolved ignition will take place. *Perchloric acid* if misused or in concentrations greater than 72% can be extremely dangerous. The rate of burning of organic substances is greatly increased by contact with perchloric acid. Strong dehydrating agents cause the acid to decompose and explode violently. Perchloric acid should be stored away from other chemicals in a noncombustible storeroom and protected against freezing temperatures. Large volumes of water are recommended for fire fighting.

*Oxides.* The reaction of oxides with water may evolve sufficient heat to ignite combustible material. Under certain conditions lime slaking can cause ignition of paper or wood. Oxides should be kept on skids in a dry, fire-resistive storeroom. If water is used to fight fire in the vicinity of quicklime or other oxides, care should be taken not to wet them. When lime has been wet, it is essential to remove it from the building and thoroughly wash the building with large volumes of water.

*Inorganic peroxides* are noncombustible, but, because of their reaction with water to liberate oxygen and heat, they may cause ignition of nearby combustible material. Storage in moisture-tight metal drums and segregation in a fire-resistive storeroom are recommended for fire-safe storage.

*Chlorates.* When mixed with combustible material, chlorates may cause that material to ignite or explode spontaneously. Storage should be in a noncombustible area away from combustible material and acids. Water is the best extinguishing agent for fires in the vicinity of chlorates. *Perchlorates* have similar fire-hazard properties to chlorates. They are explosive on contact with concentrated sulfuric acid.

*Dusts (q.v.).* The possibility of explosion of dust suspensions in air is the principal hazard of dust and is present in any plant where combustible dust is created during operating processes. The two principal factors influencing explosion severity are the rate of pressure rise and the maximum pressure developed. These differ for different dusts. Dusts have been classified according to relative explosibility (24).

Serious dust explosions have occurred during starch manufacture and use, sugar refining, in woodworking plants, during sulfur crushing, rubber recovery, in metal-dust plants, fertilizer plants, textile plants, and many other industries. Recommendations

to prevent dust explosion include good housekeeping, building construction to prevent dust accumulations on ledges and beams, dust collecting and removal systems, elimination of possible sources of ignition, use of inert gas to prevent ignition in grinding equipment, and provision of adequate vents in the building and equipment to prevent formation of dangerous explosion pressures. Fundamental principles for the prevention of dust explosions and detailed recommendations for those industries where the dust hazard is severe have been prepared (17).

*Materials Subject to Spontaneous Heating.* Many substances are dangerous because they react with light, air, water, or other chemicals to produce heat. A familiar example of spontaneous heating is cotton rags containing linseed oil. If the rags are bunched together in a warm corner, where heat cannot be readily dissipated, ignition is likely. Charcoal, particularly if fresh and made from hard wood, is subject to spontaneous heating and ignition. Hay, grains, feed and manure, wet sawdust, and finely divided metals including iron, cobalt, nickel, and uranium are subject to spontaneous heating. For a detailed list of materials subject to spontaneous heating, as well as precautions and other pertinent information, see reference (19). Because the factors influencing spontaneous heating vary for different materials, it is not feasible to make general recommendations for its prevention. Ventilation, temperature, moisture content, and presence of foreign materials are factors that must be considered in evaluating the spontaneous-heating hazard of a particular material.

### Building Construction

The governing factor in the design of fire-safe buildings should be the building types and construction material that will avoid loss of life due to inferior construction or lack of protection for occupancy hazards. The ideal structure is one in which the amount of combustible material in any one fire area is small, and the construction is such that fire in one section cannot spread to another, and exposure fires cannot enter the building. Good fire prevention and fire protection for any building starts on the drafting board, and where hazardous occupancy conditions exist, such as those frequently found in chemical plants, these conditions must be taken into account by the architect.

The possibility of explosion is so great in many plants handling organic chemicals that an ideal structure for such an occupancy is one having just enough walls and roof to keep out the weather. Many industries conducting hazardous processes are erecting equipment in the open to prevent accumulation of flammable vapors and to minimize the damage should an explosion occur in the equipment. Control equipment for outside operations is usually located in small buildings. If the hazardous process is to be conducted within a building, a one-story fire-resistive structure is recommended.

**Heights and Areas.** The height and area of a building should be limited to reduce the life hazard from fire and to restrict the maximum extent of fire to a degree commensurate with the facilities of the public fire department. Building codes commonly contain restrictions on maximum heights and areas of buildings of different types of construction and different classes of occupancy. There is wide variation in the limits in the various codes so that local codes should be consulted to assure compliance. Although large areas are commonly permitted in one-story buildings, it is not good practice to permit excessive areas because of the danger of fire in the contents even in fire-resistive buildings. Another objection to excessive areas is the difficulty usually encountered in complying with exit requirements.



**Fire Walls and Party Walls.** Area limitations are expressed in terms of areas between exterior walls, party walls, or fire walls. Where a building is divided into sections by one or more fire walls, each section is considered independently in application of area limitations. To be effective, a fire wall must have sufficient fire resistance and stability to withstand the effects of the most severe fire that may be expected to occur in the building, and it must provide a complete barrier to the spread of fire with all openings protected against such spread. Fire walls must extend through and above combustible roofs.

**Protection of Openings.** All openings in walls, partitions, and floors should be protected as a safeguard to life and for the prevention of fire spread. Elevator- and stair-shaft enclosures should be built of fire-resistive material with all openings protected by fire doors. Openings around pipes and other small floor and wall openings will permit vertical and horizontal fire spread if not eliminated. To prevent horizontal spread through openings in fire walls, fire doors designed to give high resistance to fire and heat are provided. For emergency exits, doors must swing with the direction of travel. When doors are normally open, it is customary to use horizontally sliding doors. When doors are normally closed, a swinging door is preferred. Counterbalanced doors are available for freight-elevator shafts (19).

**Exits.** Exit requirements are determined by the degree of combustibility of a building, the fire hazard of its contents, the amount of fire protection provided, and the maximum number of people expected to occupy the building. Detailed exit requirements will be found in the Building Exits Code (12). Minimum requirements call for at least two means of escape for every area in the building where people congregate. Arrangement of exits is such that if fire or smoke cuts off one means of escape the other will not be affected. The maximum distance to be traveled to reach the nearest exit varies with the type of occupancy, usually ranging from 75 feet in high-hazard occupancies to 150 feet in places of public assembly located at street level. The size of an exit is customarily measured in units of width representing the space needed for one file of people, each unit being 22 inches wide. Two units of width per exit is a minimum requirement except for stairways serving less than 50 persons. Factors influencing the width of exits from an area include the maximum number of persons that may normally be found in the area, the floor on which the area is located, and the degree of fire hazard of the occupancy.

### Fire-Extinguishing Means

The fire defense of a chemical plant is provided by both public and private fire protection. Public fire protection consists of fire department equipment and manpower, a fire alarm system, and water supply. One or more forms of private protection are essential to facilitate prompt detection and extinguishment of fire. Automatic detection equipment, watchman protection, fire brigades, automatic sprinklers, special fixed extinguishing systems, and first-aid extinguishers are types of private protection applicable to the chemical industry. Because of the special hazards involved, many chemical plants rely almost entirely on private fire protection for fire control.

**Automatic Detection Equipment.** Delayed detection of fire is one of the principal factors responsible for loss of life and extensive property damage. It is for this reason that automatic detection equipment, which provides a means of early detection of fire, is a particularly desirable feature of private protection. There are two types of detec-

tion devices. The *fixed-temperature device* operates at a temperature that could only be caused by heat from fire in the area protected. The *rate-of-rise device* operates when the temperature in the area protected rises at a rate faster than a predetermined safe rate. Devices of either type are usually placed on or near the ceiling and located in respect to fire hazards so that they will operate promptly in case of fire. A closed electric circuit is commonly used to connect these devices to a local fire alarm or to a public or private fire alarm office.

**Watchman Protection.** A watchman who makes at least hourly trips through a plant over a predetermined route and whose tour is supervised by one of various available methods offers another reliable means of detection. The watchman must be intelligent, able-bodied, and well trained, and his route must take him to all hazardous areas. The importance of strict adherence to these requirements is apparent when it is remembered that for 16 of the 24 hours of each day the fire safety of many plants is entirely in the hands of the watchman.

**Fire Brigades.** Private brigades are maintained to extinguish fire before it gets beyond control or to hold it in check until the public fire department arrives. In certain localities where public protection is nonexistent or weak, sole responsibility for manual fire protection of a plant rests with its private brigade. Depending on the size of the plant, brigade personnel may be employed as full-time firemen or may be volunteers regularly employed at other jobs. To be effective, brigades must command the respect and confidence of management and employees, must be adequately trained and equipped, and must be immediately available at all times.

**Automatic Sprinklers.** An automatic sprinkler system that incorporates the two most important features of fire control—prompt detection and prompt extinguishment or control—is universally recognized as a major feature of private fire protection because of its excellent record of performance. Records indicate that automatic sprinklers control 96.1% of all fires in areas where they are installed. Closed water-supply valves and explosion-damaged systems are the principal causes of the small number of unsatisfactory performances in the chemical industry.

An automatic sprinkler system consists of pipes, usually suspended from the ceiling, through which water is conducted to sprinkler heads attached to the pipes at regular intervals. A sprinkler head contains a half-inch opening normally kept closed by a disk until fire occurs. One of several types of mechanical devices to keep the disk in place consists of a metal lever held against the disk by solder that melts at 160°F. Heat rising from a small fire melts the solder, allowing water to flow through the head against a deflector causing a heavy spray to be thrown in all directions.

**Special Fixed Extinguishing Systems.** *Foam extinguishing systems* which deposit a layer of foam over burning material are desirable for the protection of many processes in the chemical industry. Foam is generated by mixing equipment as needed, and conducted by piping to outlets. Apparatus handling flammable liquids and large outdoor storage tanks are suited for foam protection. The effectiveness of foam protection depends upon the proportion of water and foam-producing material, the rate of foam application, and the quality of the foam. See also *Foams*.

**Carbon Dioxide Systems.** Systems have also been devised to discharge carbon dioxide gas automatically or manually. Flammable liquids in open containers, ovens, dryers, and electrical equipment are some of the hazardous areas that can be protected by carbon dioxide. The system consists of discharge outlets in the fire area connected by piping to a supply of carbon dioxide stored under high pressure at normal tem-

peratures, or at lower pressures under refrigeration. The system can be operated automatically by a heat-sensitive device in the fire area.

**Water Spray Systems.** Water spray is widely used to protect chemical-process equipment and storage tanks of flammable liquids and gases. Many chemical plants have installed water spray systems not only for the extinguishment of fires, but also for control where water spray cannot normally extinguish fires but can serve to keep the equipment cool, prevent explosions, allow the closing of valves for the control of the flow of escaping flammable liquids, and allow time for the assembly of extinguishing equipment of the blanketing or smothering type, such as foam, carbon dioxide, or dry chemical. In water spray systems, water is broken up into small drops and discharged as a spray by special types of nozzles. Characteristics of the hazard to be protected, size and velocity of the water particles, location of nozzles, and volume of water discharge required are some of the factors that must be considered in designing water spray protection (19).

**Fire extinguishers** are portable devices, containing a limited supply of fire-extinguishing medium, that are designed to cope with fires in their earliest stages. Their provision is considered necessary even though the property may be equipped with automatic sprinklers and other fixed fire-protection equipment. Adequacy of a first-aid fire appliance depends upon suitability for use on the type of fire anticipated, sufficiency of the number and capacity, accessibility, quality of maintenance, and employee familiarity with its use.

Each type of first-aid appliance is of value, but all are not equally effective in extinguishing the three general classes of fires. For *Class A fires* in ordinary combustibles the cooling effect of water or of solutions containing a large percentage of water is of first importance. Recently, aqueous solutions of wetting or penetrating agents, sometimes called "wet water," have been used in fighting fire, but they have not yet been generally accepted. For *Class B fires* in flammable liquids, grease, etc. a blanketing or smothering effect is preferred. *Class C fires*, those involving live electrical equipment, require a nonconducting extinguishing agent. Table I, below, indicates suitability and other pertinent information about the various types of first-aid extinguishers.

**Pump Tank Extinguishers.** These consist of 2½- or 5-gallon tanks with a built-in hand-operated pump and with hose and nozzle attached. The extinguishing agent is plain water. If the extinguisher is exposed to freezing temperature, a calcium chloride solution is used. A calcium chloride charge containing a corrosion inhibitor should be obtained from the extinguisher manufacturer for this purpose.

**Gas Cartridge Extinguishers.** These extinguishers contain 2½ gallons of plain water, which is expelled by the pressure of carbon dioxide. The gas is released from a cartridge into the container by inverting the extinguisher and bumping it on the floor to puncture the gas-retaining seal.

**Soda-Acid Extinguishers.** This type of extinguisher comes in various sizes, the most common being the 2½-gallon size. The extinguishing agent is a water solution of sodium bicarbonate. Concentrated sulfuric acid is held in the extinguisher near the top in a glass bottle closed by means of a loosely fitting lead or ceramic stopper. When the extinguisher is inverted, the sulfuric acid mixes with the sodium bicarbonate solution, producing carbon dioxide in sufficient quantity to build up pressure to expel the solution from the extinguisher.

**Foam Extinguishers.** See discussion on "Fire fighting" under article titled *Foams*.

**Loaded Stream Extinguishers.** There are two types of loaded stream extinguishers.

In both the extinguishing agent is an alkali metal salt solution whose exact composition is a trade secret. One type uses carbon dioxide from a cartridge to expel the solution. In the other, gas pressure developed by reaction between an acid and the alkali metal salt solution is the expelling force. The solution differs from other extinguishing solutions in that it extinguishes the flame rather suddenly and there is a notable fire-retarding effect. There is no smothering vapor produced, but apparently there is a chemical reaction tending to inhibit oxidation.

TABLE I. Facts About Fire Extinguishers.

Type	Effect	Use on fires of class:			How to operate	Recharge	Protection from freezing
		A	B	C			
<i>Plain water:</i>							
Pump tank	Cooling	Yes	No	No	Hand pump	After use	Approved antifreeze chemicals may be added to the water
Gas cart- ridge	Cooling	Yes	No	No	Invert, bump on ground	After use	—
<i>Water and chemicals:</i>							
Soda-acid	Cooling	Yes	No	No	Invert	Annually	Keep in heated cabinet if building is unheated
Foam	Cooling, smothering	Yes	Yes	No	Invert	Annually	Never add antifreeze chemicals
Loaded stream	Cooling and "oxidation-inhibiting"	Yes	Yes	No	Invert, bump on ground	After use	None required to $-40^{\circ}\text{F.}$
<i>Chemical:</i>							
Vaporizing liquid	Smothering	"	Yes	Yes	Hand pump	After use	None required to $-50^{\circ}\text{F.}$
Carbon dioxide	Smothering	"	Yes	Yes	Open valve at top	After use	None required
Dry chemical	Smothering	"	Yes	Yes	" <sup>b</sup>	After use	None required

<sup>a</sup> Only small surface fires.

<sup>b</sup> See directions on extinguisher.

*Vaporizing Liquid Extinguishers.* These extinguishers come in various sizes and contain a vaporizing liquid extinguishing agent which may be expelled by a hand pump in the extinguisher, by stored pressure using carbon dioxide gas, or by stored pressure using air as the expelling agent, depending on the design of the extinguisher. The most common extinguishing agent is a specially treated, electrically nonconducting liquid consisting largely of carbon tetrachloride with components added to lower the freezing temperature to  $-50^{\circ}\text{F.}$  and to prevent corrosion. Several other liquids have been used in recent years as extinguishing agents. Chlorobromomethane and methyl bromide are two of these; use of the latter is restricted because of its toxic and corrosive properties.

*Carbon Dioxide Extinguishers.* The extinguishing agent is carbon dioxide stored under 800–900 p.s.i. at normal room temperatures. The extinguisher is essentially a pressure container equipped with a valve and a discharge horn. A tube extends from the valve to the bottom of the extinguisher so that only liquid carbon dioxide reaches

the horn until about 80% of the contents is discharged. Extinguishers vary in capacity from 2 to 25 lb. of carbon dioxide.

*Dry Chemical Extinguishers.* The extinguishing agent is primarily sodium bicarbonate with materials added by the extinguisher manufacturer to make the dry chemical water-repellent and free-flowing. Capacities range from 4 to 30 lb. of dry chemical. The smaller extinguishers contain a cartridge of carbon dioxide as the expelling agent. Wheeled units are equipped with a cylinder of nitrogen.

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Aluminum and Magnesium with Certain Chlorinated Hydrocarbons," No. 34; "Limits of Flammability of Methyl Ethyl Ketone Vapor in Air at Initial Temperatures of 100, 150, and 200°C.," No. 38; "The Comparative Explosion Hazard of Ammonium Nitrate containing Organic Matter" (also supplement to this Bulletin), No. 39; "The Lower Limit of Flammability and the Autogenous Ignition Temperature of Certain Common Solvent Vapors Encountered in Ovens," No. 43; Chicago.

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C. I. BABCOCK, JR.

## FIRE-RESISTANT TEXTILES

It is probable that the ready combustibility of cellulosic materials, including wood and the vegetable fibers, has been a source of concern since man's discovery and utilization of fire. It is known that as early as the 4th century B.C. attempts were made to reduce the combustibility of wood by treatment with vinegar (9). This early attempt at flameproofing represents a type of trial-and-error experimentation of which numerous other examples are reported in the literature from that time until the 19th century, when the first systematic investigation of flame retardants seems to have been undertaken. While the early efforts to render cellulose noncombustible appear to have been directed principally toward wood, the emphasis since the 17th century has been placed on vegetable fibers and the textile products made therefrom. Gay-Lussac conducted his studies, reportedly at the behest of Louis XVIII, on linen and hemp fabrics, in which he deposited from solution a considerable number of different salts (8). Later studies included cotton fabrics, and as the importance of this fiber increased, cotton textiles became the chief subject of flameproofing studies. In recent years, flame retardants have been developed principally for cotton, the rayons, and for other cellulose derivatives such as cellophane. Textile fabrics made from wool, silk, and the proteinlike synthetic polymers are not considered sufficiently combustible, in most cases, to warrant the use of flame-resistant finishes.

Historically, the development of fire retardants for textiles has passed through four stages, the products of which form the basis for classifying today's retardants in four categories. The earliest developments, which stemmed first from trial-and-error experimentation, and later from systematic studies, resulted in the class of water-soluble or nondurable fire retardants. The next development involved deposition of insoluble retardants within the fabric—this was a natural outgrowth of the work on water-soluble materials. Studies on both water-soluble retardants and insoluble deposits have been carried on concurrently since about 1850. The third significant advance in the science of flameproofing was the use of mixtures of halogenated organics and insoluble metal salts and oxides. While this innovation was not introduced until the early 1930's, it was in time to provide a new class of fire retardants that proved of considerable military importance during World War II. The fourth stage in the development of fire retardants began in the late 1930's, and now appears to offer most promise for future development. It is based on the chemical combination of the fire retardant and cellulose molecules.

Although the ideal fire-resistant fabric may never be achieved, chemical modifications of cellulose may approach it more closely than has heretofore been possible. The ideal fire-resistant fabric (1) should not contribute fuel to either flaming or flameless combustion; (2) should retain its flame-resistant properties under all conditions

to which it may be subjected; (3) should not be altered in its normal fabric characteristics, including hand, drape, absorbency, dyeing and dye-fastness, strength, and durability; (4) should not have acquired, through the treatment, such adverse properties as toxicity, abnormal mildew susceptibility, or discoloration; and (5) should cost relatively little more than an unfinished fabric.

None of the fire-resistant fabrics available today is considered satisfactory in all of the characteristics listed above, and many of them are unsatisfactory in the majority of those characteristics. On the other hand, several of the available finishes compensate somewhat for their disadvantages by adding to the fabric other desirable characteristics such as water resistance, mildew resistance, weather resistance, and resistance to shrinkage. After a review of the mechanisms by which cellulosic fabrics are rendered fire-resistant, several of the better finishes typical of each classification will be considered in some detail, and their properties discussed.

### Definitions

A brief glossary of some of the more commonly used terms is presented here; definitions more specific and limiting for a number of the terms will be found in the many specifications for fire retardants and fire-resistant fabrics.

*Flameproofing*—a convenient term widely used in reference to processing, to fire or flame retardants, or to the general field of activity. For example, flameproofing process, flameproofing solution, or flameproofing of textiles. It is not considered correct to refer to a finished fabric as "flameproof."

*Fire-resistant fabric*—a fabric that will not support a flame and will have a limited period of glow (flameless combustion) after an igniting flame is removed.

*Flame-resistant fabric*—a fabric that will not support a flame.

*Glow, afterglow*—the incandescent flameless combustion of a fabric. Glowing usually follows flaming, but may result from ignition by a cigaret butt, flatiron, etc.

*Fire retardant*—a material that will give textile fabrics the property of fire resistance.

*Flame retardant*—a material that will give textile fabrics the property of flame resistance.

*Glow retardant*—a material that will give textile fabrics the property of glow resistance.

*Durable finish*—a very loose term that implies a degree of permanence or durability under exposure to certain conditions of use, such as laundering or weather exposure. For durability to have any real meaning, the condition of exposure must be rigidly specified.

### Action of Fire Retardants

It is not likely that any single mechanism can account for the action of fire retardants in modifying or inhibiting the combustion of cellulose, since it appears that different retardants act by different mechanisms, and in some cases by a combination of mechanisms. Four functions of fire retardants have been postulated and are generally conceded to constitute the most satisfactory explanations of flameproofing action, since individually or collectively they seem to encompass most of the observed facts.

**1. Chemical Mechanisms.** The influence of fire retardants on the rate of formation and the relative amounts of the various decomposition products of cellulose is the

basis of chemical theories of flameproofing action. It is generally assumed that the chemical changes in the composition of the reaction products themselves are not significant.

When a cellulosic fabric burns, the decomposition usually takes place in two stages. First, a sufficient volume of combustible gases is evolved so that a flame is supported; the heat of the combustion causes the flame to travel over the surface of the unburned fabric and raises its temperature so that more gases are continuously supplied as a support for the flame. Following the flame, as the second stage of the reaction, is the slower oxidation of the carbonized residue of fabric structure. This

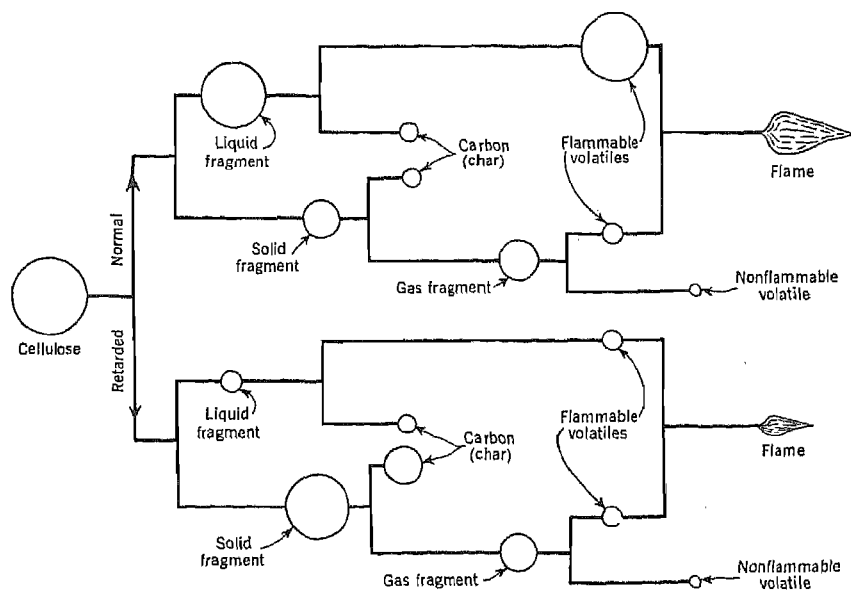


Fig. 1. Thermal degradation of cellulose in the presence and absence of retardants (7).  
(The sizes of the circles represent approximate quantities of the various products)

secondary oxidation, or glowing, normally continues until the entire fabric is reduced to a light, fluffy ash. Even if the flame becomes extinguished, the glowing may continue beyond the charred portions of the fabric and slowly consume the unburned cellulose. The course of the two-stage decomposition of cellulose has been carefully studied and the reaction products of the combustion have been examined (7). During combustion, cellulose decomposes rather heterogeneously into liquid fragments and solid fragments. As the reaction progresses the liquid fragments, or tars, are further decomposed into a carbonaceous char and flammable gases. The solid fragments decompose into an additional amount of char, and into volatile gases, a part of which are flammable and a part nonflammable. The flame is supported by the flammable gases from the decomposition of both solid and liquid fragments, with gas production from the liquid fragments greatly exceeding that from the solid phase.

Cotton that has been treated with an effective fire retardant gives substantially the same decomposition products upon burning as does untreated cotton, but the proportion of tar is sharply reduced, and the amount of solid char is correspondingly increased. Therefore, as the decomposition proceeds, there is a much smaller amount



of flammable gas available from the tar, and larger amounts of nonflammable gases from the decomposition of the char fraction. The total amount of flammable gases is not sufficient to support flaming. See Figure 1.

Char oxidation is also inhibited by an effective fire-resistant finish. The elimination of this afterglow, like the prevention of afterflaming, is considered a catalytic effect of the fire-retardant chemicals. It is presumed that the principal effect of glow-retardant chemicals is to direct the oxidation of carbon to carbon monoxide rather than to carbon dioxide. The former reaction liberates only 26.4 kg.-cal. per mole as against 94.4 kg.-cal. per mole for the complete oxidation to carbon dioxide. The oxidation to carbon monoxide is not sufficiently exothermic to maintain the afterglowing of the cellulose char.

Measurements have been made of the amounts of carbon monoxide, carbon dioxide, water, hydrocarbons such as methane, tar, and char formed in the pyrolysis of fabrics treated with a wide variety of chemicals. The reduction of tar and the consequent increase of char have been considered by some workers to be an indication of flame-retarding efficiency, and the ratio of carbon monoxide to carbon dioxide as an indication of glow retardancy. There are, however, a sufficient number of agents that do not behave as they should according to this assumption, so that it must be concluded that additional mechanisms play a significant role in developing fire resistance in cellulosic products.

**2. Coating Mechanisms.** A number of the effective flame retardants melt or fuse at temperatures approaching the combustion temperature of cellulose, and it has been suggested that the fused chemicals may coat the fibers so that further combustion or support of a flame is prevented. The coating is thought to exclude oxygen from the cellulose, and at the same time cut down the escape of flammable gases.

There are a number of flameproofing agents, of which the borophosphate complexes are an outstanding example, that fuse and bubble to such an extent under the application of heat that it is difficult to doubt that the coating mechanism is at least partly responsible for the fire-retardant action. However, in many cases, there is little evidence of any fusing or coating mechanism, and, moreover, the amount of applied flame retardant is often too small for a coating action to seem a reasonable explanation of its function. The additional fact that a number of chemicals fuse readily to form relatively effective fiber coatings, and yet remain ineffective as fire retardants, seems to indicate that coating action is, at best, only one mechanism by which fire resistance may be achieved.

**3. Gas Mechanisms.** Since flaming results from the combustion of gases, considerable attention has been given to the manner in which fire retardants affect the gases released during the burning of cellulose. Most fire retardants for cellulose increase the amount of water vapor formed during combustion, and some also increase the amount of carbon dioxide, while reducing the production of carbon monoxide and hydrocarbon gases. The net result of these changes is, of course, an increase in noncombustible gases and a decrease of flammable gases. Still further amounts of noncombustible gases are produced in the decomposition of retardants that yield ammonia, carbon dioxide, water, and hydrogen chloride or hydrogen bromide.

It is probable that the release of nonflammable gases contributes to flameproofing action by diluting the flammable gases sufficiently so that a flame cannot be supported, or by actually smothering the flame. However, there is evidence which argues against placing too great an emphasis on the function of noncombustible gases in developing

fire retardancy. For example, a fabric may be coated with a rather heavy deposit of chlorinated paraffins, plus a catalyst for the formation of hydrogen chloride from the resin and also of water from the cellulose, and little fire retardancy will result. On the other extreme, some very effective flame retardants release no nonflammable gases themselves, cause a relatively minor increase in the production of water vapor, and actually increase the ratio of carbon monoxide to carbon dioxide.

**4. Thermal Mechanisms.** The view has been proposed that flame retardants may act to dissipate the heat of combustion of cellulose, so that the temperature is kept below the critical level at which flaming can continue. It is suggested that this action of the chemicals is due in part to the endothermal nature of the changes that take place near the flaming temperatures, and in part to the action of the chemical in conducting heat away from the point of burning. In partial rebuttal of this theory, it has been demonstrated that some effective fire retardants actually undergo an exothermal reaction at combustion temperatures, and that, in any case, a great many effective flame retardants are present in insufficient amounts to support the belief that any important heat-conducting action might take place.

### Types of Fire Retardants

#### NONDURABLE FINISHES

**Materials.** The amount of a fire retardant that must be deposited on a fabric to prevent flaming and glowing is a measure of the efficiency of the retardant (see Table I). The efficiencies of various water-soluble fire retardants as reported on that basis by a number of authors show generally good agreement. In some cases, mixtures of two or more salts have been found much more effective than any one of the components used by itself. For example, an add-on of 60% of borax is required to prevent fabric-

TABLE I. Amount of Retardant Required to Prevent Flaming and Glowing (Nondurable Finishes).

Flame and glow resistance		Flame resistance only	
Retardant	Minimum add-on, % <sup>a</sup>	Retardant	Minimum add-on, % <sup>a</sup>
Ammonium bromide, $\text{NH}_4\text{Br}$ .....	7	Sodium vanadate, $\text{Na}_3\text{VO}_4$ .....	2½
Ammonium molybdate, $(\text{NH}_4)_2\text{MoO}_4$ .....	7	Lithium hydroxide, $\text{LiOH}$ .....	5
Sodium tungstate, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ .....	9	Sodium molybdate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ .....	6
Diammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$ ....	12	Potassium hydroxide, $\text{KOH}$ .....	8
Phosphoric acid, $\text{H}_3\text{PO}_4$ .....	12	Ammonium metavanadate, $\text{NH}_4\text{VO}_3$ .....	9
Zinc chloride, $\text{ZnCl}_2$ .....	12	Sodium hydroxide, $\text{NaOH}$ .....	10
Ammonium iodide, $\text{NH}_4\text{I}$ .....	14	Sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ..	12
Calcium chloride, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ .....	14	Potassium nitrate, $\text{KNO}_3$ .....	13
Magnesium chloride, $\text{MgCl}_2$ .....	16	Potassium carbonate, $\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ ..	16
Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$ .....	18	Arsenic acid, $\text{H}_3\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ .....	20
Sodium stannate, $\text{Na}_2\text{SnO}_3$ .....	18	Sodium phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ..	20
Sodium aluminate, $\text{NaAlO}_2$ .....	19	Potassium permanganate, $\text{KMnO}_4$ .....	22
Sodium silicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ .....	20	Sodium bicarbonate, $\text{NaHCO}_3$ .....	23
Ammonium chloride, $\text{NH}_4\text{Cl}$ .....	22	Potassium thiocyanate, $\text{KSCN}$ .....	25
Ammonium borate, $\text{NH}_4\text{BO}_3$ .....	24	Potassium phosphate, $\text{K}_3\text{PO}_4$ .....	27
Sodium bisulfate, $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ .....	30	Potassium dihydrogen phosphate, $\text{KH}_2\text{PO}_4$ .....	30
Sodium arsenate, $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ .....	33	Sodium selenite, $\text{Na}_2\text{SeO}_3$ .....	36
Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .....	60		

<sup>a</sup> Parts by weight added per 100 parts fabric.  
Source: reference (8).

flaming, and boric acid, by itself, is ineffective as a flame retardant even in amounts which equal the weight of the fabric. When a mixture of seven parts of borax and three parts of boric acid is used, however, a fabric may be given satisfactory fire resistance with as little as 61½% add-on.

In general, the more efficient salts or mixtures are selected for use because they have less effect on the hand, drape, flexibility, and tear strength of the fabric than retardants that require higher fabric add-ons. Other considerations influence the selection of retardants, however, and different textile products may demand different finishing treatments. For the same add-on, the stiffening effect of fire-retardant salts and mixtures varies considerably. Some effective retardants, such as phosphoric acid, cannot be used because they cause fabric deterioration. Others may not have the necessary solubility characteristics, or may promote mildew on the fabric, lack glow resistance, volatilize gradually, or be too expensive.

The water-soluble fire retardants most widely used achieve their effects by one or more of the following mechanisms: (1) They fuse and form a foam which coats and protects the fabric from further combustion; (2) they release mineral acids that alter the ratios of cellulose decomposition products; or (3) they release large amounts of non-combustible gases or vapors. Examples of (1) are the borax - boric acid mixtures and boric acid with diammonium phosphate. The acid phosphates and sulfamic acid,  $\text{NH}_2\text{SO}_3\text{H}$ , are good examples of (2). Ammonium bromide, ammonium sulfamate,  $\text{NH}_2\text{SO}_3\text{NH}_4$ , and hydrated sodium carbonate are salts that yield substantial amounts of nonflammable gases. Among the retardants that have seen fairly wide usage for textiles and that act by one or more of the mechanisms listed above, are the following: (1) borax - boric acid (7:3); (2) borax - boric acid - diammonium phosphate (7:3:5); (3) sodium phosphate - boric acid (1:1); (4) boric acid - diammonium phosphate (1:1); (5) borax - boric acid - sodium phosphate (10:7:3); (6) ammonium sulfamate; (7) ammonium sulfamate - diammonium phosphate (3:1); (8) ammonium bromide; (9) sodium tungstate; and (10) borax - boric acid - sodium phosphate - sodium tungstate (15:47:18:20). Less commonly used, but finding application in products where special requirements of hand, drape, or transparency make other materials unsuitable, are the following types of finish: (11) sulfamates of urea or other amides and amines; (12) aliphatic amine phosphates (for example, triethanolamine phosphate); (13) phosphamic acid (monamidophosphoric acid),  $\text{NH}_2\text{PO}_3\text{H}_2$ , and its salts; and (14) alkylamine bromides, phosphates, and borates.

**Methods of Application.** The water-soluble fire retardants are the most easily applied of the textile flameproofing agents. The process involves merely the impregnation of the fabric with a water solution of the retardant, followed by drying. Adjustment of the solution concentration and regulation of the fabric wet pick-up control the amount of retardant deposited in the fabric. Textile piece goods may be processed on a finishing range consisting of any convenient means of impregnating the fabric with the solution, such as a padder or dip tank (see *Dyes (application)*), followed by drying on cans or in an oven. Water-soluble fire retardants may be applied by spraying or brushing, by dipping textile articles such as clothing or drapes, or as a final rinse in commercial or home laundering.

**Characteristics of Treatment.** The better water-soluble fire-resistant finishes, when properly applied, possess most of the qualities that would be desired in the ideal fire retardant, except for durability. They add little to the fabric weight, do not affect its color or its tensile strength, and have only a slight effect on hand, flexibility,

and drape. They are inexpensive and very easy to apply, either to piece goods or manufactured articles. Tear strength is usually lowered, although this reduction can be kept within reasonable limits. Glow resistance is satisfactory with the better formulations. Formulations that have not been carefully worked out or that have been improperly applied are likely to cause stiffening of the cloth and severe loss in tear strength, and may volatilize or migrate, promote the growth of mildew, or catalyze the degradation of the cellulose.

#### INSOLUBLE DEPOSITS

**Inorganic Materials.** The principal disadvantage of water-soluble fire retardants—lack of durability—has prompted an extensive study of various insoluble deposits or precipitates. Many patents have been issued since 1850 covering insoluble salts, oxides, hydroxides, and combinations thereof deposited within fabrics, and several processes have had some commercial use.

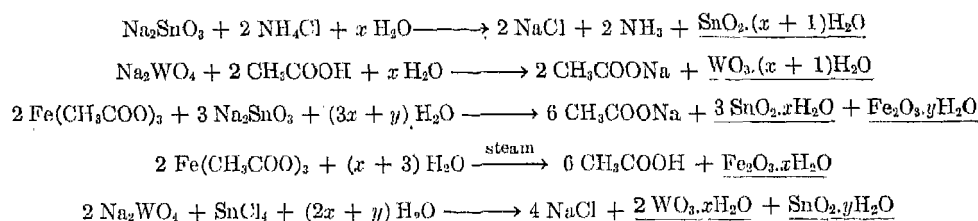
The relative efficiencies of a number of insoluble inorganic deposits have been studied (8); several of them are listed in Table II with the minimum percentage that must be added to the fabric to provide fire or flame resistance.

TABLE II. Amount of Retardant Required to Prevent Flaming (Insoluble Deposits).

Retardant for flame resistance	Minimum add-on, %	Retardant for flame resistance	Minimum add-on, %
Ferric oxide, $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ .....	19	Antimony oxychloride, $\text{SbOCl}^a$ .....	30
Stannic oxide, $\text{SnO}_2$ .....	20	Zinc stannate, $\text{ZnSnO}_3$ .....	40
Lead monoxide, $\text{PbO}$ .....	21	Tin tungstate, $\text{SnWO}_4$ .....	50
Manganese dioxide, $\text{MnO}_2$ .....	22	Aluminum tungstate, $\text{Al}_2\text{WO}_6$ .....	54
Ferric chromate, $\text{Fe}_2(\text{CrO}_4)_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ ..	24	Antimony trioxide, $\text{Sb}_2\text{O}_3$ .....	79
Lead chromate, $\text{PbCrO}_4$ .....	37		

<sup>a</sup> Also gives glow resistance.  
Source: reference (8).

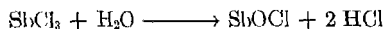
In many textile uses it is desirable to employ a retardant that does not color the fabric, and this places a limitation on the insoluble deposits which can be used. Limitations are also imposed by the degrading effect that some deposits, such as antimony oxychloride, have on cellulose. Because of the deficiencies of single insoluble deposits, two or more are often used as codeposits. Several of the treatments which have found some acceptance are listed below (the reactants are given, and among the products the insoluble compounds are underlined):



Unlike many mixtures of water-soluble salts, codeposits of insoluble materials simply produce the combined effect of the individual deposits, and in no case show a flameproofing efficiency greater than the separate ingredients themselves. Glow resistance, however, is improved in many cases by the addition of insoluble deposits

which by themselves provide no resistance to flaming. The last example above provides both flame resistance and glow resistance, at least initially. It has been observed that the deposits that are responsible for glow resistance are less insoluble than the flame-resistant materials and are therefore more quickly removed in laundering or weathering.

*Commercial Processing.* There are several methods for introducing the insoluble deposits into the fabric structure. The one most generally used is the multiple-bath method, in which the fabric is first impregnated with a water-soluble salt or salts in one bath, and then passed into a second bath which contains the precipitant. In another method the reactants (or one reactant) are dissolved in a nonpolar solvent, and after the fabric is saturated with that solution, the solvent is removed by drying and the fabric is passed through a water bath. Ionization and precipitation of the insoluble forms then take place within the fabric. The double-bath type of reaction has been illustrated by the equations above. An example of the second method of application is the treatment of a fabric with antimony trichloride dissolved in methanol, after which the fabric is passed into water where the antimony trichloride hydrolyzes to the oxychloride.



In another treatment, zinc chloride is dissolved in ethylene glycol monoethyl ether (Cellosolve), and borax in diethylene glycol monoethyl ether (Carbitol). The two solutions are mixed and used to impregnate the fabric. Upon exposure to water, zinc borate is precipitated in the fabric. The advantage claimed for the method is the elimination of multiple baths for decomposition of the soluble salts.

*Characteristics of Treatment.* Insoluble deposits are not extensively used as textile flame retardants, for the following reasons: (1) They are inefficient fire retardants (in comparison to water-soluble agents) and therefore more material must be added to the fabric, increasing both the cost and the deleterious effects on the fabric's properties. (2) They generally give very poor resistance to afterglow. (3) Many of them affect the color, strength, light resistance, or other properties of the fabric. (4) Durability to weathering and laundering has not been sufficiently high to meet the requirements of many uses. (5) Application techniques are frequently complicated and therefore expensive. (The durability of the fire resistance, and particularly the glow resistance which they provide, is not sufficient to outweigh their disadvantages.)

**Organic Materials.** Since 1930 a number of water-insoluble organic materials have been proposed as flame retardants for textiles. For the most part these have been halogenated aliphatics or aromatics, or combinations of the two. Polychlorinated naphthalene, chlorinated diphenyls, chlorinated paraffins, chlorinated rubbers, vinyl resins, and other chlorine-containing organics have been suggested (see also *Chlorine compounds, organic*). A number of brominated compounds have also been advanced, since bromine is known to be an effective ingredient of fire-retardant compositions. For the most part, organic materials when used by themselves are relatively inefficient fire retardants. In a few cases, where the add-on has been as great as 50–60% of the fabric weight, some flame resistance is provided, but at the expense of the hand, texture, pliability, etc., of the fabric.

Recently a number of organic phosphates have been found to be relatively effective as fire retardants. Organic amine phosphates and their polymers offer some promise as flameproofers, although most of these materials are still being studied.

Excellent results have been obtained from a resin of brominated allyl phosphate. Relatively low polymers of this material, probably not much more than tetramers, can be applied to cotton or rayon fabrics and have been found to be very durable to laundering and to weathering. While there is the possibility that this material forms a phosphate ester of cellulose, the general opinion is that in this case such a change does not occur, and therefore the brominated allyl phosphate has been listed as an insoluble organic deposit.

#### CHLORINATED ORGANIC-METAL OXIDE TYPE

A class of fire retardants that proved of military importance during World War II developed from finishes based on insoluble deposits. Chlorinated rubber and chlorinated naphthalene had been used alone or in conjunction with water-soluble retardants (11), but an improvement was effected by depositing them as an afterfinish on fabrics in which insoluble metallic oxides had already been deposited by the double-bath method (10). A practical one-step process for this type of flameproofing treatment soon followed. This was based on the discovery that effective fire resistance results from merely mixing insoluble fire-retardant salts or oxides with a chlorinated organic vehicle, forming a suspension in the solvent, and applying the paintlike mixture to fabrics (12).

There are innumerable variations of the chlorinated organic-metal oxide type of finish. Chlorinated paraffins are the most commonly used vehicles, a relatively hard 70% chlorinated paraffin resin often being plasticized by the liquid 42% chlorinated material. Chlorinated rubber is often used where it is desirable for the fabric to have a "dry" hand, and vinyl resins have been utilized to a lesser extent. Small amounts of nonchlorinated organic resins are sometimes added to the vehicle to give special properties of hand or feel, and plasticizers such as tricresyl phosphate are also used occasionally.

Antimony oxide is almost invariably one of the principal ingredients of the "dry solids" part of the fire-retardant mix, although the antimony sulfides, arsenic oxide, tin oxide, zinc borate, and other materials can be used. In addition to antimony oxide, the dry solids usually include an acid acceptor such as calcium carbonate, and color pigments. The function of the acid acceptor is to neutralize any hydrogen chloride that may be gradually released during storage or weathering of the treated fabric. Mildew-inhibiting agents may be incorporated in either the vehicle or the dry solids part of the mix.

A typical fire-retardant mix of the chlorinated organic-metal oxide type is shown in Table III. The zinc oxide is used as a glowproofing agent, a function which zinc borate will also perform.

**Commercial Application.** The chlorinated organic-metal oxide type of finish is applied as a one-step process. Preparation of the fire-retardant mix is similar to paint manufacture, in that the pigments or dry solids are first stirred into the vehicle, and then further wet-out or "ground" in a ball mill or by passage through a roller mill. Following the thorough wetting and dispersion of the dry solids in the vehicle, a petroleum solvent is added in tanks equipped with rotary or propeller-type stirrers. The application to fabrics simply involves passage of the fabric through a suitable dip tank containing the fire-retardant mix, scraping or squeezing off the excess mix, and drying to remove solvent.

The chlorinated organic-metal oxide treatment has been the subject of many

TABLE III. Fire-Retardant Mix of the Chlorinated Organic-Metal Oxide Type.

Chlorinated paraffins.....	60%	} .... Vehicle solids 50%	} .... Total solids 50%	
Plasticizer.....	20%			
Film-forming resin.....	20%			
Antimony trioxide.....	35%	} .... Dry solids 50%		
Calcium carbonate.....	20%			
Color pigments.....	30%			
Zinc oxide.....	5%			
Mildewicide, etc.....	10%			
Solvent.....			50%	

modifications, both in the constitution of the mix and in the methods of application. The mix may be prepared as an emulsion, so that the expense and fire hazard involved in the use of petroleum thinners are reduced. It may also be prepared with little or no thinner and applied to the fabric by coating techniques. The retardant may be packaged in cans and drums, like paint, and applied to fabrics by brushing or spraying.

**Characteristics of Treatment.** "FWWMR," for fire, water, weather, and mildew resistance, has frequently been used as an abbreviation for the chlorinated organic-metal oxide treatment. The combination of chlorinated organic and metal oxide contributes fire resistance, the organic binder acts to seal the fabric to water, the colored pigments protect fabric and finish from the destructive effects of solar radiation, and a mildew-inhibiting agent (which is usually incorporated) prevents rotting of the fabric. The FWWMR finish does not decrease the tensile strength of fabrics, although a poorly formulated finish may accelerate strength loss on weathering, and finishes with a relatively large proportion of dry solids may reduce tear strength. Hand, drape, flexibility, and color are more affected by the FWWMR finish than by most other types of fire retardant. The added weight to cotton fabrics ranges between 25% and 60%, averaging close to 45%. Cloth cannot be dyed after application of the FWWMR finish, and the colors of previously dyed fabrics are covered by the finish. The finish tends to be stiff in cold weather, and in some cases, sticky in hot weather. The color pigments are subject to "crocking" or rubbing off unless adequate film-forming resins are used. The durability of the finish, properly formulated and applied, is excellent. Fabrics treated with the chlorinated organic-metal oxide finish have retained their flame-resistant properties after 4-5 years' outdoor exposure. Resistance to glowing is generally lower after outdoor exposure.

The finish is not considered suitable for clothing or most interior textile decorations for homes and buildings, but for outdoor use is reasonable in price and satisfactory in performance.

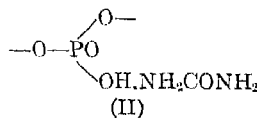
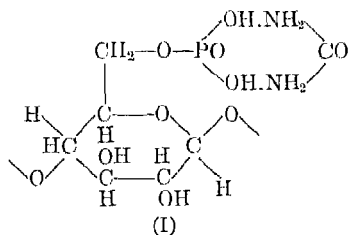
### Chemical Combinations with Cellulose

A chemical bond between the molecules of fire retardant and cellulose should produce a finish that resists the effects of laundering and weathering better than mere physical deposits of a retardant within the fabric, yarn, or fiber. A more effective distribution should also result from combination of the retardant with cellulose than is the case with physical deposits which often tend to agglomerate or build up on a "seed." The better distribution of the combined retardant, and its chemical linking to the cellulose, might reasonably be expected to permit the maximum influence of the retardant on the mechanism of cellulose decomposition.

Partial chemical modification of cotton is usually accomplished by esterification or etherification of the cellulose at accessible sites. Both the primary and secondary hydroxyls of cellulose may react with alkyl or aryl compounds, or with certain mineral acids. Mild swelling may be employed to increase the accessibility of the hydroxyls in amorphous regions of the cellulose and on (but not within) the crystallites. The swelling also permits the introduction of larger substituent groups.

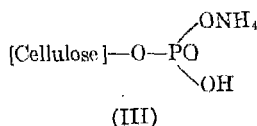
**The Urea-Phosphate Type.** The effectiveness of phosphoric acid as a fire retardant, as evidenced by a number of water-soluble phosphate salts in common use, is also observed in the phosphate derivatives of cellulose (7,13). Phosphoric acid alone effectively flameproofs cellulose, but direct phosphorylation degrades cellulose to such an extent that the method is impractical. In the presence of urea, however, cellulose will combine with phosphoric acid without undue degradation to form a fire-resistant product. One explanation of this effect is that urea acts both as a buffer for the phosphoric acid and as a swelling agent for the cellulose.

The primary hydroxyl of the cellulose should be the most easily esterified, but the substitution may take place on any of the three hydroxyls, to form either the mono-ester (I) or the disubstituted ester (II), which may be on one glucose anhydride unit or cross-linking two units.



The basic principle of this finish, according to one theory, is the reaction between cellulose and a polybasic acid in the presence of a buffer and a swelling agent which provides anhydrous reaction conditions. Phosphoric acid and urea seem to produce the best results, but satisfactory products may also be obtained with other acids of phosphorus, with ammonium phosphate, phosphamic acid, sulfuric acid, and sulfamic acid. A number of amines also may be used, including melamine, guanidine, diacyandiamide, biuret, formamide, and acetamide.

At least one other mechanism has been suggested for the reaction of phosphoric acid, urea, and cellulose to form a fire-resistant product. It is held that diammonium pyrophosphate,  $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$ , is formed by the reaction between phosphoric acid and urea, and that this salt reacts with cellulose in the presence of urea. The product is the ammonium orthophosphate of cellulose (III).



Whether the product is cellulose urea phosphate or cellulose ammonium phosphate, its activity as an ion-exchange medium has proved a disadvantage, since it loses its fire-resistant properties in the exchange of urea or ammonia by metal ions. Phosphorylated fabrics laundered under alkaline conditions will lose their fire resistance



through replacement of the ammonium ions by sodium ions. When the fabric is treated with ammonia or acid, the sodium ions in turn are replaced by ammonium or hydrogen ions and the fabric is again fire-resistant.

One solution to the problem of ion-exchange activity is to adjust the time-temperature conditions of the reaction to favor the formation of the nonionic amide rather than a salt. Another approach is in the use of more complex amines or amides which increase the bulk of the salt and thus decrease diffusion rate. A still further possibility which is commercially utilized is the formation of protective polycondensations of urea, or other amides or amines, with formaldehyde.

*Commercial Processing.* Fabrics to be treated with the urea-phosphate type of fire retardant should be as free as possible from sizing, waxes, pectins, or other impurities that might interfere with the reaction between the cellulose and the fire-retardant solution. For best results fabrics are desized, thoroughly scoured with caustic soda, bleached, and preferably mercerized before the flameproofing process. Dyeing or printing should also be done before the fire-resistant finish is applied. The flameproofing solution itself can be prepared by mixing the acids and nitrogen compounds together in cold water, or by first heating these ingredients so that they will react. The solution is most conveniently padded on the fabric in a two- or three-roll mangle, using a heavy squeeze to give a wet take-on of 75–100%. The fabric is then dried, preferably on a tenter frame, or on cans. Following the drying operation, the fabric is cured or baked for three to fifteen minutes at temperatures in the range of 325–350°F. Finally, the fabric is washed thoroughly in hot and cold water to remove the unreacted soluble materials, and then it is dried again.

*Characteristics of Treatment.* The urea-phosphate type of fire-retardant finish increases the fabric weight by about 15%, but has no serious adverse effect on the hand and drape characteristics of the fabric. Colors of dyed or printed goods are affected somewhat, although not seriously. Tensile strength may be lowered by 20–50%, although by carefully controlled processing the strength loss can be kept at the low end of this range. Tear-strength losses generally exceed losses in tensile strength. The fire-resistant properties of the finished fabric will withstand repeated laundering with neutral soaps and nonionic detergents. Laundering with strong ionic detergents, however, will destroy the flame-resistant properties through ion exchange, and laundering with strongly alkaline detergents will saponify the cellulose phosphate ester. The simpler types of urea-phosphate fire-resistant fabrics are most suitable for indoor fabric decorations and for clothing that can be laundered under mild conditions. A number of the improved finishes will successfully retain their fire resistance after some weather exposure. The cost of the finish is relatively high compared to either the water-soluble type or the chlorinated organic-metal oxide type, a factor which tends to restrict wide commercial application.

**Titanium Complexes.** Cotton and rayon textiles may be durably flameproofed with treatments based on the (presumed) reaction of cellulose with acids of titanium and antimony (6). It is believed that the durability of this type of fire retardant depends in part on the two secondary valences of titanium which, with the four primary valences, give a coordination number of 6. These secondary valences may be directed toward —O— or —OH groups in the cellulose molecule, giving chelated structures.

Titanated cellulose alone has not sufficient fire resistance to be of practical interest. When cellulose is treated with a solution containing both titanium oxychloride and

antimony trichloride, however, effective flame resistance having considerable stability to water is imparted. Fabrics treated in this manner are reported to have retained their flame-resistant properties after one hundred household launderings. This durable flame resistance is believed to be due to a chelated compound of titanium and cellulose (containing also antimony), one glucose unit of which may be represented as  $C_6H_9O_6Ti(OH)_2OSb(OH)_2$ . While this treatment provides excellent resistance to flaming, it does not prevent afterglow to the extent desirable. Resistance to afterglow can be improved by padding the fabric with sodium silicate before treatment with titanium oxychloride and antimony trichloride. When the metal chlorides are applied, silica is precipitated within the fabric and effects the improvement in glow resistance.

In the treatment of cotton or rayon fabrics with titanium compounds such as titanium oxychloride, titanium oxysulfate,  $TiOSO_4$ , and other acid salts, the fiber-swelling action of the titanium compounds is an important factor, since the swelling increases the accessibility of the cellulose to the reactants. Titanium oxychloride has proved a more effective swelling agent than titanium oxysulfate.

*Commercial Processing.* The titanium oxychloride-antimony trichloride solution contains several per cent excess hydrochloric acid for stability, necessitating acid-resistant finishing equipment for the first steps in applying the treatment to fabrics. The cloth is preferably desized, scoured, and bleached before treatment; vat dyeing also usually precedes flameproofing. Direct dyes are sometimes, although not always, applied after the fire retardant, which affects somewhat the shade of both direct and vat dyes, necessitating care in the selection of the dyes to be used. The retardant itself is best applied from a 3-roll double-dip rubber-lined padder, using a heavy squeeze to assist penetration of the solution and to keep the wet pick-up in the neighborhood of 80%. Following impregnation a scray or J box is employed to give a time lag of one to fifteen minutes for additional penetration. The fabric is then neutralized in soda ash, washed, soaped, washed, and dried.

*Characteristics of Treatment.* Cotton and rayon fabrics processed by the titanium-antimony system generally have more body and are somewhat less limber than the unfinished cloth. To a large extent hand can be controlled by the afterseour. Tensile strength is not significantly affected, although tear strength is usually reduced measurably. Porosity and absorbency are not greatly altered by the inorganic treatment, which adds from 12 to 15% to the weight of the fabric. The finish is not proof against repeated laundering with relatively strong alkali followed by fluoride sours. The finish cannot be classed among the low-cost types, partly because of the nature of the chemicals used, and partly because of the special equipment required for its application.

**Other Titanium-Antimony Finishes.** Treatments based on titanium chloride acetate and antimony trichloride have also given good results when applied to cotton and rayon fabrics as fire retardants. In these treatments a semidrying immediately after the padding step is recommended. This reduces the wet pick-up from about 80 to 30-35%, concentrating the retardant solutions in the fabric. The material is then neutralized and washed.

### Test Methods

The problem of evaluating the combustibility of textiles has resulted in the development of more than a score of test methods, some of which are accepted as standards

by various governmental organizations and technical societies. These test methods differ in the size of the fabric sample used, the preparation of the sample for test, the position of the sample during burning, the method of ignition, and the method of recording and interpreting the results. Each of the methods, however, falls into one of two classes of burning tests (1) fire-resistance tests—methods for measuring the resistance of treated textiles to flaming or to flaming and glowing; and (2) flammability tests—methods for measuring the rate of burning of textile fabrics, or their relative flammability. Since so many methods and devices have been used for measuring both fire resistance and flammability, only the method in each category most widely used in the U.S. will be described.

**Fire-Resistance Tests.** The fire-resistance test method which has gained greatest acceptance in this country is frequently referred to as the "vertical burning test," although it is only one of the many tests in which the fabric is suspended vertically. The method described here has been incorporated into a great many specifications, among which are CCC-T-191a (Federal), CCC-D-746 (Federal), 6-345 (Army), 24-C-20 (Navy), and others. In this test a  $12 \times 2\frac{1}{2}$ -in. strip of fabric is suspended vertically so that the lower edge hangs just  $\frac{3}{4}$  in. above the top of a Bunsen or Tirrell burner. The burner is adjusted to give a  $1\frac{1}{2}$ -in. luminous flame, so that  $\frac{3}{4}$  in. of the fabric extends into the flame. After an ignition time of 12 seconds the flame is removed and the duration of continued flaming of the fabric is timed, as well as the duration of the afterglow and the length of the charred area. Most of the specifications allow an after-flaming maximum of 2 seconds and an average char length (10 strips) of  $3\frac{1}{2}$  in., with a maximum of  $4\frac{1}{2}$  in. for any one strip. In some cases the duration of afterglow is limited to a specified time.

The above description refers only to the essential features of the method. Numerous refinements have been adopted which are intended to make the results highly reproducible. These include the standard draft-free cabinet, methods of conditioning the specimens, special fabric clamps and holders, manometers to control the flow of gas to the burner, and techniques for measuring char length. The reproducibility of the test as a measure of flame resistance is generally superior to its reproducibility on measurements of char length or glow time.

**Flammability Tests.** The rate of burning of a fabric is usually highly dependent on the position of the fabric during burning. A fabric vertically suspended and ignited on the bottom will burn with considerably more rapidity than one held in a horizontal position. The speed with which vertically suspended fabrics burn makes distinctions among fabrics difficult, and for that reason many flammability testers mount the fabric specimen at some angle from the vertical position. The method described here uses a specimen inclined  $45^\circ$  from the vertical.

The tester known as the A.A.T.C.C. or inclined flammability tester was developed after World War II and has been more widely used than any other rate-of-burning device. In this method, a  $6 \times 2$  in. strip of fabric is clamped in a rack inclined at  $45^\circ$ , and the surface of the fabric near the bottom is exposed to the flame of a microjet burner for a period of one second. If the sample is ignited by this flame, the time of flame travel over 5 in. of the specimen is used as an indication of the relative flammability of the fabric.

The burning rate of many fabrics is extremely sensitive to the handling and preparation which the fabric receives before being mounted in the tester, as well as to the fabric moisture content, the ambient humidity, and variations between samples.

The limitations of the A.A.T.C.C. method and other flammability testers have been discussed in the literature (2).

**Additional Tests.** In the complete evaluation of fire-resistant textile fabrics, many tests in addition to those for determining fire resistance or flammability are employed. These include strength tests, toxicity tests, mildew tests, tests for durability to laundering, weathering, storage, heat, and a number of measurements on such properties as flexibility, crocking, and hand. Since most of these are standard methods for measuring textile properties, they will not be described here.

### Uses of Fire-Resistant Textiles

Fire-retardant finishes for textiles are applied almost exclusively to cotton and rayon textiles. A small amount of jute brattice cloth is made fire-resistant for use in mines, and occasionally kapok fiber is given a fire-resistant treatment for certain military uses. There are few examples in which linen has been processed for fire resistance, since it is not commonly used in articles which are considered to represent a potential fire hazard. The noncellulosic textiles, as noted, are not considered sufficiently flammable to warrant the use of a fire-resistant finish.

While cotton and rayon fabrics exhibit approximately the same degree of flammability, the flameproofing of cotton is much more common than that of rayon because: (1) cotton is more commonly used where exposure to fire is likely, and (2) cotton fabrics are more adaptable to rigorous finishing processes than rayon fabrics. Cotton is used almost exclusively in many outdoor, military, and industrial textile items which frequently require fire-resistant properties. The principal outdoor uses include tents, awnings, tarpaulins, truck and boat covers, and other special-purpose protective fabrics for both civilian and military use.

The indoor uses of fire-resistant textiles are chiefly in curtains and drapes, upholstery, and other decorative furnishing fabrics. Clothing items utilize relatively small amounts of fire-resistant textiles because the majority of clothing articles are not considered unduly hazardous and because none of the available finishes is considered wholly satisfactory for clothing from price and quality standpoints (3). A few special types of clothing, mostly costume items, which because of their construction are specially susceptible to burning, are processed with a fire retardant. Other special-purpose garments such as welders' and steel workers' coveralls, fire fighters' clothing, and certain types of military clothing are often considered to need fire-resistant properties.

There are uses of textiles in which fire resistance is mandatory. Many of these uses are military, but the number of civilian uses in which fire-resistant properties are demanded is increasing. State and municipal regulations and ordinances are mediums through which these requirements are extended to textiles. Outdoor uses in which fire resistance is mandatory are confined for the most part to tents which are used as places of public assembly. Indoor uses include curtains and drapes, decorative fabrics, and sometimes upholstery and floor coverings in hotels, night clubs, hospitals, and other public buildings.

A greater use of fire retardants and fire-resistant textiles will undoubtedly result from improvement in the properties of the retardants and the treated fabrics, and a reduction in the cost of the treatments. It is expected that there will be an increase in the number of states and cities which require fire-resistant properties in certain textile uses, and that the scope and severity of present restrictions will also increase.

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G. S. BUCK, JR.

FIREWORKS. See *Pyrotechnics*.

## FIRST AID

First aid is defined as the immediate, temporary treatment given in case of accident or sudden illness before the services of a physician can be secured (4). It should therefore be considered as emergency treatment and not as a substitute for a physician's care.

This article makes no attempt to describe treatments for the numerous possible injuries caused by the many chemical and mechanical agents employed in so diverse a field as the chemical industry. It is suggested that a trained chemist, safety engineer, or physician prepare a first-aid chart adapted to the needs of the plant. Modifications of the first-aid kits listed in Table I and the bibliography given below should prove helpful in the preparation of these charts. (See also *Industrial hygiene and toxicology; Safety and safety practices*.)

TABLE I. Contents of Two Commercial First-Aid Cabinets.

Mine Safety Appliances Co. Industrial first-aid cabinet	Fisher Scientific Co. Laboratory first-aid cabinet
2 oz. mild tincture of iodine	4 oz. 5% acetic acid soln.
2 oz. boric acid soln.	4 oz. 1% ammonia
2 oz. castor oil	4 oz. aromatic spirits of ammonia
2 oz. aromatic spirits of ammonia	4 oz. 3% hydrogen peroxide
2 oz. Activol soap	1 oz. 3½% tincture of iodine
2 oz. Foille for burns	6 oz. milk of magnesia
1-in. adhesive compresses	4 oz. mineral oil
2-in. compress bandages	1 oz. oxidized turpentine
4-in. compress bandages	3 oz. boric acid powder
40-in. triangular bandages	1 oz. copper sulfate
5 yd. ½-in. adhesive plaster	2 oz. egg albumin
5 yd. 1-in. adhesive plaster	4 oz. mustard (powdered)

TABLE I. (Concluded).

Mine Safety Appliances Co. Industrial first-aid cabinet	Fisher Scientific Co. Laboratory first-aid cabinet
1 in. × 6 yd. gauze roller bandages	4 oz. sodium bicarbonate
2 in. × 6 yd. gauze roller bandages	4 oz. sodium hydrogen phosphate
3 in. × 6 yd. gauze roller bandages	4 oz. sodium thiosulfate
Absorbent cotton	2 oz. tannic acid
Absorbent gauze	1 oz. tartar emetic
Sterilized gauze	1½ oz. sterile Vaseline petroleum jelly
Cotton wound applicators	3 oz. universal antidote
Wood tongue depressors	6 amyl nitrite capsules
Wood splints	Boric acid ointment
Finger cots	Butesin pierate ointment
Tourniquet	½-in. adhesive tape
Eye cup	1-in. roll bandages
Medicine glass	3-in. roll bandages
Eye dropper	4 oz. sterile cotton
Spoon	3-in. square sterile gauze
Safety pins	Wood applicators
Scissors	Tourniquet
Tweezers	Eye cup
	Scissors
	Spoon
	Tweezers

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**FISCHER-TROPSCH PROCESS.** See *Fuels, synthetic liquid*.

**FISETIN**,  $C_{16}H_{10}O_6$ . See *Dyes and dye intermediates*, Vol. **5**, p. 352.

#### FISH AND SHELLFISH

The annual catch of fish throughout the world averages about 30,000,000,000 lb. Table I summarizes the quantity of fish caught in the countries that operate the most important commercial fisheries. The same types of fish are caught along the European coasts as along the North Atlantic coast of the United States and Canada, and the European fisheries and fish-handling methods resemble those of the eastern North American areas. Extensive fisheries are operated in various Asiatic countries. In many of these areas, owing to lack of extensive canning and refrigerating facilities, the fisheries are conducted on a more primitive basis. Salting and sun drying are the principal preservation methods used in such areas.

In the U.S. one of the largest fisheries is carried out in the North Atlantic with principal landings being made at Gloucester, Boston, and nearby ports. The most common species are rosefish, haddock, and cod, all nonoily species which hold up well in cold storage and hence are frozen in large quantities, usually after cutting of bone-free fillets and packaging. The principal species of fish canned in the New England area is herring. Small fish of this species are caught in waters adjacent to Maine and are canned as sardines. Lobster and clams are the most important shellfish produced

TABLE I. Estimated Annual Fish Production.

Country	Year	Volume of catch, <sup>a</sup> billions of pounds	Country	Year	Volume of catch, <sup>a</sup> billions of pounds
U.S. (including Alaska).....	1948	4.58	Spain.....	1947	0.50
Japan.....	1947	3.54	Union of South Africa..	1947	0.44
U.S.S.R.....	1933	2.9	France.....	1947	0.34
China.....	1936	2.8	Portugal.....	1947	0.32
India, Persia, and Burma....	1932	2.0	Germany.....	1937	0.31
Korea.....	1937	1.4	Newfoundland.....	1947	0.31
Norway.....	1947	1.34	Poland.....	1935	0.30
United Kingdom.....	1947	1.23	Netherlands.....	1947	0.28
South and Central America..	1937	0.7	Denmark.....	1947	0.23
Canada.....	1947	0.61	Sweden.....	1947	0.18
Iceland.....	1947	0.53	Italy.....	1947	0.14

<sup>a</sup> Round weight as landed.

Source: Figures reported for the year 1947 were taken from *The State of Food and Agriculture for 1948*, Food and Agricultural Organization, Washington, D.C., September 1948. Other statistics were compiled from a variety of sources.

in the New England area, although there is also a moderate production of scallops and oysters. Fisheries of eastern Canada resemble those of the New England area.

Along other parts of the Atlantic coast of the U.S. farther to the south, production of shellfish and crustaceans is more important than that of other food fishes. In the Chesapeake Bay states, oyster and crab production is of greatest importance, while along the coast of the Gulf of Mexico, shrimp and oysters are the most important species.

Along the Pacific coast of North America, tuna, salmon, pilchard (known also as California sardine), and halibut are the most important species. The tunas are caught in part off the coast of California (albacore tuna as far north as British Columbia), but large quantities are caught off the coast of Central America, frozen aboard the fishing vessel, and returned to canneries in California and Oregon. Alaska is the location of the principal salmon species, although fairly sizable catches are also made in British Columbia waters, in Puget Sound, Washington, and at the mouth of the Columbia River. A part of the pilchard catch is canned in California as sardines. Halibut are taken in the North Pacific, principal landings being at Ketchikan and other adjacent Alaskan ports, at Prince Rupert, B.C., and Seattle.

Two species of fish are caught in huge quantities for nonfood use. These are menhaden caught along the Atlantic, and pilchard on the Pacific coast. In excess of a billion pounds of these fish are rendered annually into fish oil for industrial use and fish meal, which is used for animal feed (principally for poultry). (See *Fats and fatty oils*.) Certain fishery by-products are also manufactured. Vitamin A oils made from shark and other fish livers are the principal source of natural vitamin A. Fish meal and oil are recovered from trimmings from fish canneries and from fish-fillet plants. Some other by-products include amino acids, histamine, and synthetic "egg white" from fish flesh; leather and glue from fish skins; cholesterol, squalene, and lecithin from fish oils; pearl essence and charcoal from fish scales; isinglass from fish sounds (air bladders); and protamine for use with insulin from milt. Table II gives information supplied by the Fish and Wildlife Service concerning some of the principal species of fish produced in the U.S. for food (22).



## Composition of Fish

Fish flesh usually has the following approximate composition: oil plus water, 80%; protein, 18%; ash, 1.3%; other miscellaneous substances, 0.7%. The moisture and oil contents of fish flesh are inversely proportional and hence their sum is quite close to 80%. The oil content varies more than any other constituent of fish flesh. Some species have an average oil content of less than 1%, while others average as much as 20%; the oil content of individuals of the same species may vary as much as fifteen-fold. As a general rule, species of fish in which the flesh has a high oil content have livers with a low oil content and vice versa. The following species, which may be described as nonoily, contain as a rule less than 2% oil in the flesh: cod, flounder and "sole," haddock, pollock, rockfish, sea trout, whiting, clams, crabs, oysters, and shrimp. The following species, having as a rule between 2 and 6% oil in the flesh, may be considered to be of an intermediate classification: alewives, croaker, halibut, mullet, chum salmon, pink salmon, and tuna. The following species which can be classified as very oily contain more than 6% oil in the flesh: herring, mackerel, men-

TABLE II. Production of Principal Species of Fish in the U.S.

Species	Annual catch, 1946, <sup>a</sup> 1,000,000 lb.	Annual value, 1946, <sup>a</sup> \$1,000,000	Principal producing area	Season of fishery	Principal markets
Cod.....	103	6.7	New England	Year around	Fresh and frozen
Croaker.....	47	4.7	Middle Atlantic	Year around	Fresh
Flounder and "sole".....	123	10.3	New England	Year around	Fresh and frozen
			Middle Atlantic	Year around	Fresh and frozen
			Pacific Northwest	Year around	Fresh and frozen
Haddock.....	155	13.0	New England	Year around	Fresh and frozen
Halibut.....	55	11.1	Pacific Northwest	May to July	Fresh and frozen
			Alaska	May to July	Fresh and frozen
Herring, lake.....	20	0.9	Great Lakes	Year around	Fresh
Herring, sea.....	284 <sup>b</sup>	3.2	Maine, Alaska	April to Dec.	Canned (sardines)
Mackerel.....	106	5.1	New England	May to Dec.	Fresh
			Middle Atlantic	May to Dec.	Fresh
			Southern Calif.	June to March	Canned
Mullet.....	43	4.6	South Atlantic	Year around	Fresh
Rosefish.....	178	7.7	New England	Year around	Fresh and frozen
Salmon.....	478	31.9	Alaska	May to Nov.	Canned
			Pacific Northwest	May to Nov.	Canned
Sea trout.....	47	4.9	Middle Atlantic	April to Nov.	Fresh
Tuna.....	222	26.6	California, Oregon	Year around	Canned
Whiting.....	65	1.6	New England	May to Oct.	Fresh and frozen
Clams.....	46	11.3	New England	Year around	Fresh
			Middle Atlantic	Year around	Fresh
			Pacific Northwest	Year around	Fresh
Crabs.....	147	12.7	Middle Atlantic	Year around	Fresh
			South Atlantic	Year around	Fresh
Oysters.....	80	26.1	Gulf	Sept. to April	Fresh
			Middle Atlantic	Sept. to April	Fresh
Lobster.....	24	9.5	New England	Year around	Fresh
Shrimp.....	192	21.4	Louisiana	Year around	Canned and fresh

<sup>a</sup> Data are for 1946 except for the portion of the catch taken in the South Atlantic and Gulf States which are for 1945.

<sup>b</sup> About one-third is canned or salted and two-thirds is used for the production of meal and oil.

haden, coho salmon, sockeye salmon, king salmon, sablefish, and pilchard. See also references (17,19).

The protein content of fish usually is quite close to 18% and the amino acid make-up of fish proteins is well balanced with respect to the essential amino acids (*q.v.*), there being no deficiency of any important amino acid. The principal minerals occurring in fish are calcium, copper, iron, magnesium, phosphorus, potassium, sodium, chlorine, and sulfur. Relatively large amounts of iodine, fluorine, and arsenic also occur, the last two in organic combinations that do not give rise to toxic effects.

Fish flesh is a good source of most of the vitamin B complex, and fish viscera (and fish meal made from fish trimmings or whole fish) are an excellent source of vitamin B<sub>12</sub>, the animal protein factor, riboflavin (*q.v.*), and thiamine (*q.v.*). Vitamin C occurs in fair amounts in fish roe. Many fish livers are an excellent source of vitamin A, and livers from some species are also a source of vitamin D. (See *Fish-liver oils*; *Vitamins*.)

In addition to the substances listed many others occur in fish in small amounts. Trimethylamine oxide, (CH<sub>3</sub>)<sub>3</sub>NO, occurs in salt-water fish as an excretory product analogous to urea. In sharks, urea occurs in appreciable quantities in the flesh. Glycogen occurs in living fish muscle, but upon death of the fish it is converted largely to lactic acid. The acidity of fish flesh is close to neutral in the living fish. Upon development of lactic acid the pH falls to about 6.0 (as low as 5.8 in some species such as salmon) and then, as basic spoilage products such as ammonia and trimethylamine accumulate, a rise in pH to values between 7 and 8 usually takes place. Oysters contain a great deal more glycogen than other species of fish, so that the pH drops slowly during spoilage to pH values as low as 4.8.

Fish oils are characterized by a relatively high proportion of unsaturated fatty acids, present as triglycerides (1). Saturated acids make up only about 25% of the total acids present. Most of the unsaturated acids are C<sub>16</sub> (principally palmitoleic), C<sub>18</sub> (principally oleic with some octadecatrienoic), C<sub>20</sub>, and C<sub>22</sub> acids. Fish oils contain appreciable quantities of cholesterol, lecithin, and smaller quantities of glycerol ethers such as batyl alcohol (glycerol  $\alpha$ -ether of octadecyl alcohol). A hydrocarbon, squalene, C<sub>30</sub>H<sub>50</sub>, containing 6 double bonds, is a common constituent of many fish oils. (See also *Fats and fatty oils*; "Marine-oil acids" under *Fatty acids*.)

Fish meal and fish solubles are important items of commerce, especially in the field of poultry feeding, and their composition has an important bearing on their nutritive value (see *Feeds, animal*). Fish meals have greatly varying composition depending not only upon the species of fish and source of raw material but also upon the method of manufacture. Ordinarily, the moisture content of commercial fish meals varies between 6 and 12%. However, manufacturers attempt to keep the moisture content below 10%. Ash content usually runs between 10 and 20% but may be somewhat higher when the meal is made from fillet waste containing a high proportion of bone. Protein content of fish meal generally varies between 55 and 70%. Oil content of meals usually varies from 2 to about 15%. Fish meal is an important source of animal protein factor, and fish-liver meals may contain as much as 10 micrograms of animal protein factor per gram of meal.

Condensed fish solubles are of more uniform composition than are fish meals. A typical concentrated fish soluble will have the following general composition: moisture, 50.0%; total solids, 50.0% (crude protein, 33.9%; fat, 2-6%; and ash, 9.4%). Content of principal vitamins of such a concentrate expressed as micrograms per gram is: thiamine, 4.0; riboflavin, 20.0; nicotinic acid, 325; calcium pantothenate, 40.0;

choline, 4000; biotin, 0.14; pyridoxine, 0.0125; and vitamin B<sub>12</sub>, about 0.3. Content of individual amino acids of such a concentrate is as follows: arginine, 4.3%; histidine, 5.8%; lysine, 4.9%; leucine, 4.7%; isoleucine, 2.7%; valine, 3.0%; phenylalanine, 2.3%; tryptophan, 0.35%; methionine, 1.5%; threonine, 2.4%; cystine, 0.6%; and glycine, 4.1%. Condensed fish solubles have a specific gravity of about 1.20 at 20°C. and a pH of 4.5–5.0.

### Handling and Processing

**Fresh Fish.** Constant maintenance of a low temperature during handling of fish is the most important factor in prolonging keeping quality. Bacteria associated with fish are of types that thrive at the body temperature of the fish, which is only a few degrees above the freezing point of water. Hence it is of much greater importance for fish to be kept close to 0°C. than is the case with other flesh foods. Fish are usually iced at sea immediately after capture. Upon arrival at shore, fish are generally unloaded by means of baskets or tubs lowered by a boom into the hold of the fishing vessel. When forks are used to unload the fish, care is taken that the tines pass only through the head to avoid spread of bacteria into the edible flesh.

Fish that are to be filleted are first washed, usually in a large rotary cylindrical washer fitted with sprays of water. The tumbling action of the washer also removes scales. The fish then pass along a conveyer belt to the fillet line, where the fillets are cut by hand, after which they are skinned and packed for distribution or freezing. Some plants are now equipped with machines which mechanically cut fish fillets from the fish. Another mechanical device recently introduced is a fish-skinning machine; this device is also adaptable to splitting thick fillets into cuts more readily utilized by the consumer.

**Frozen Fish (2).** The degree of change in fish muscle brought about by the freezing process is determined by the rate at which the temperature of the fish is brought from about  $-1$  to  $-7^{\circ}\text{C}$ . If freezing is extremely rapid (that is, such as takes place when a microtome slice of fish is immersed in a liquid bath at  $-50^{\circ}\text{C}$ .), the water in the fish freezes almost instantly as extremely small crystals within the cells, and when such a sample is thawed it exactly resembles the original flesh as to texture and appearance. When fish is frozen very slowly (as when a large halibut is placed in still air at  $15^{\circ}\text{F}$ .) the formation of ice crystals occurs at such a slow rate that the crystals build up by migration of water from one part of the flesh to another. When such fish is thawed the water is not re-absorbed completely and large histological and even considerable macroscopic changes of texture and appearance occur which result in a deteriorated quality. In commercial practice quick freezing leads to a product that is not markedly different from a slow-frozen product, because the rate of freezing is actually not extremely rapid owing to limitations in equipment.

Most of the adverse changes sometimes encountered in frozen fish result not from any change brought about by the freezing process itself but rather through changes during storage of the frozen product. One such change is desiccation, caused by transfer of moisture vapor from the surface of the fish to the refrigeration pipes. The most effective method of reducing this problem is to employ jacketed cold-storage rooms in which the refrigeration pipes are entirely separate from the cold-storage room, which is surrounded by a thin layer of refrigerated air circulating to the refrigeration compartment through the outer thin jacket of the double-walled room. Such installations have

proved very successful in several large plants. More commonly an attempt is made to keep the temperature differential between the refrigeration pipes and the product at a minimum; this reduces the amount of desiccation considerably. In all cases the product is protected against moisture loss by some means. Whole fish after freezing are given a thin coating of ice (ice glaze) by immersion in cold water. Fish cuts such as fillets are packaged using moisture-vapor-proof wrappers (15). The latter are not completely impervious to moisture vapor, so that there is a slow transfer of moisture through the wrapper. An ice glaze, as long as it remains intact, affords complete protection, but it suffers limitations of cracking or peeling and also evaporates; unless replaced at periodic intervals it therefore loses all its effectiveness.

Another serious change occurring during cold storage is oxidation of fish oils and pigments resulting in development of rancid flavor and discoloration. A very minute amount of air will enable such changes to take place. Thus, packaged fish having small air voids within the package undergoes appreciable oxidation, and the amount of air passing through the best grades of moisture-vapor-proof wrappers is sufficient to cause extensive oxidation. Antioxidants have been used in some cases to minimize oxidation. Most effective reduction in oxidation, however, is obtained by keeping air away from the fish. With packaged fish this is accomplished most practically by giving the fillet an ice glaze before packaging. With some species the most unsaturated fat occurs in a thin layer just beneath the skin, and if this is removed most of the oxidation is prevented. The skin itself acts as a considerable barrier against penetration of oxygen, and where the skin is not removed oxidation is reduced.

The degree of saturation of fish oils is a much greater factor in determining whether a particular species is susceptible to rancidity than is the amount of oil present. Thus sablefish, which contain up to 20% oil of a very stable type, give no trouble with rancidity even after a year's storage, whereas pink salmon, which contain only about 6% of a highly unsaturated oil, often become rancid after 2 months' storage, and haddock, having only 0.2% of an unsaturated oil, will show some indications of rancidity after storage for 9 months to a year.

Fish are frozen commercially in either "sharp" or quick freezers. The former is a room usually containing shelves made from the refrigeration pipes. Such freezers result in a fairly slow rate of freezing, such that packaged fish require about 12 hours to freeze and the largest whole fish up to 48 hours. Quick freezers are usually of either the plate-contact type in which the packaged product is compressed between refrigerated plates or of the air-blast type in which the product is subjected in a tunnel to a rapid blast of very cold air. Quick freezing usually results in freezing of packaged fish in about 2 hours. The rate of freezing is of more importance from the standpoint of production (that is, ability to freeze a large quantity of fish in a short time) than of any great improvement in quality. Freezing of packaged fish under pressure in a plate freezer results in elimination of air voids within the package, which leads to longer storage life by reducing oxidation and desiccation within the package.

**Canned Fish.** Fish are canned by two types of processes. In one the fish is cooked and then packed into the can and processed, and in the other method the raw fish is packed into the can and a combined cooking and processing step is carried out. As examples of these two procedures the canning methods employed for tuna and salmon will be briefly described (12).

A large part of the tuna catch is brought back from distant fishing grounds in the frozen state and is first thawed, usually by immersion in tanks containing running

water. The tuna are then eviscerated by hand and placed in large wire baskets set on carts, which are rolled into steam chests where the fish are cooked for  $1\frac{1}{2}$ –8 hours (depending upon the size of the fish) at 99–104°C. The precooking removes considerable oil and some water and makes the subsequent separation of flesh from skin and bones much easier.

After cooling for about 12 hours, the cooked fish are cleaned by hand. At this stage the head, tails, fins, skin, and bones are separated, and the flesh split longitudinally to permit removal of the dark meat. The loins of white meat are then split across the grain by a guillotine-type slicer. Cans are usually filled by hand, although within recent years several automatic or semiautomatic fillers have been tried. The  $\frac{1}{2}$ -lb. tuna can (307 × 113 size) is commonly employed. Fish is graded as standard (75–85% large pieces), fancy (all large pieces), and flakes. After filling,  $\frac{1}{6}$  oz. salt and about  $1\frac{1}{2}$  oz. vegetable oil (cotton, soybean, or peanut) are added to each can, the cans are exhausted (usually in an exhaust box although some canneries use vacuum sealers), and then are seamed. Processing usually consists of retorting the  $\frac{1}{2}$ -lb. cans for 75 minutes at 115.5°C.

Five species of salmon are canned along the Pacific coast of North America. The chinook or king salmon is canned principally near the mouth of the Columbia River (at or near Astoria, Oregon). It is the largest of the five species and has a high oil content. It varies in color from fairly deep orange-red to nearly colorless. When canned it commands the highest price of all salmon species. The red salmon or sockeye is canned chiefly in the Bristol Bay area of Alaska. It has a deep red color and a fairly high oil content. The medium red or coho, the pink salmon, and the chum salmon are the three remaining species in descending order of color, oil content, and value. They are all produced principally in Alaska, most of the pink salmon being canned in southeastern Alaska. Extensive salmon canning also is carried out along the North Pacific Asiatic coast, particularly in Japan and the U.S.S.R.

Salmon are usually caught near the cannery and are landed within a few hours without ice. The fish are cleaned mechanically in a machine which cuts off the head and fins and removes viscera. After inspection and removal of any small pieces of fin, the fish are placed under rotary gang knives which slice the fish to a thickness suitable for the can size to be used. Salt is added to the empty can, which then enters the filling machine. On the Columbia River, chinook salmon are hand-cleaned and hand-packed. Cans then have lids loosely clinched and pass into the vacuum-closing machine where a vacuum is applied and the cans seamed. The usual size can (#1—1 lb., tall) requires 90 minutes at 10 p.s.i. steam pressure in the retort.

Certain fishery products, particularly crab, have a tendency to discolor when canned. Sometimes a dark black discoloration appears on the lid, bottom, or side of the can. This is usually iron sulfide which forms when sulfides are liberated from the fish during heat processing. Coating of the inside of the can with a lacquer containing zinc usually reduces this difficulty. Colorless zinc sulfide tends to form before the iron is attacked. Sometimes the product is dipped in citric or tartaric acid before canning. This lowers the pH and helps to prevent iron sulfide formation. In extreme cases parchment liners are used in the can. Often crab meat develops a blue discoloration upon canning. This results from copper, either from the crab's blood or picked up by the crab meat from processing equipment, becoming oxidized and reacting with ammonia to form the bright blue copper-ammonia complex. While there is no certain method for avoiding this blue discoloration, it is minimized by careful cleaning

and washing of the crab before canning and by avoidance of contact with copper during processing.

**Cured Fish.** Smoked fish are produced by a variety of methods (11). In general, the fish are usually first cleaned and split or otherwise dressed and then brined. This is followed by a drying of the fish to remove moisture and produce a type of surface which will absorb smoke to give a glossy "pellicle." The fish are then smoked anywhere from 3 to 5 hours for very lightly smoked products like finnan haddie to up to 2 weeks for hard-smoked fish. Except in the case of fish smoked for a very long time the principal preservation is brought about by the brining and drying. In fact, lightly smoked fish are sometimes no less perishable than fresh fish. In some smoked processes the temperature of the fish is raised during smoking to the point where the fish are cooked; this cooking destroys bacteria and adds somewhat to the keeping quality. Smoke deposits formaldehyde, cresols, phenols, and certain organic acids on the surface of the fish, and if the smoking process is prolonged as with hard-smoked fish, sufficient preservative action takes place so that the fish will keep for several weeks without refrigeration. Most smoked fish, however, require refrigeration and even so will keep for only a short time.

Salt fish are preserved primarily because of the lowered moisture content resulting from osmosis during the salting process. Fish are usually salted by the dry process, in which layers of fish and salt are alternated in a barrel or other container and the brine results from moisture from the fish. Impurities in the salt such as calcium or magnesium retard penetration of the salt into the flesh so that it is important to use a reasonably pure grade of salt.

Sun-drying of fish is employed extensively in the Orient but is not practiced to any great extent in the U.S. Salt cod is produced by a combined process of salting and drying.

### Fish By-products

Fish meal and oil are ordinarily manufactured simultaneously from such fish as menhaden and pilchard by the so-called "wet process" (3). The raw material is cooked with steam usually in continuous vertical cylindrical cookers. From the cookers the cooked flesh is conveyed into presses from which emerge the "press cake," the oil, and the "stickwater" (fish-press water). The press cake then passes into dryers which in most plants are of the direct-flame type, consisting of long vertical rotating cylinders with a gas- or oil-fired flame directed into one end. As the press cake traverses the length of the cylinder it is dried and emerges at the other end where it is ground and sacked. The mixture of oil and stickwater is ordinarily separated by centrifugals, although a few of the older plants still use settling tanks. The stickwater consists of the water cooked from the fish and condensed steam in which are dissolved water-soluble fish constituents including amino acids, mineral salts, and B complex vitamins. Formerly the stickwater was discarded, but many plants now recover a valuable feeding supplement from it which is high in vitamin and essential amino acid content. The process is one of evaporation; one commonly used process makes use of multiple-effect evaporators which reduce the moisture content to 50%. The resulting "stickwater concentrate" is the final product, which is used without further drying.

The wet process for making fish meal and oil is used where a relatively oily species of fish is available and where a large volume of raw material is encountered. With

smaller volume; a batch "dry process" is employed in which the raw material is cooked and dried in one step. Oil is then pressed out and the meal ground and sacked. This method gives a less efficient oil recovery and is employed where the chief product is the meal. It is especially adaptable where a small or irregular supply of raw material is available.

### Analysis of Fishery Products

While standard methods of analysis (for example, those of the A.O.A.C. and the U.S.P.) are applicable in most cases to analyses of fishery products, there are certain instances in which such products differ from other foods and require special consideration. Procurement of a truly representative sample of the fishery product being analyzed is of special importance, particularly when either oil or vitamin A is being determined. With the very great variability of these constituents (more than one thousandfold for vitamin A between individuals of the same species and more than tenfold between large commercial batches of the same species), it is of the greatest importance to be certain that the sample being analyzed is representative of the product about which information is desired.

Because fish oils are so highly unsaturated, they oxidize very readily and also react with other constituents of the fish. This leads to difficulty in extracting oil for its determination in fishery products. Ordinarily food products are dried in a vacuum oven before extraction with ethyl ether for an oil or fat determination. For oil determinations in fishery products it is customary to extract the wet product with acetone, remove the acetone by evaporation, and sometimes purify the residue with anhydrous ethyl ether. Such a method is especially important in determining the oil content of fish meals where values sometimes only one-half to one-fourth of the true oil content are found if the ordinary ethyl ether extraction of the vacuum oven-dried sample is carried out. Use of the acetone extraction method gives results close to the true value.

In extraction of oil from fish livers for subsequent vitamin A determination in the oil, it is necessary to carry out the liver extraction without application of heat. Ordinarily the fish livers are macerated in a Waring blender or a similar device and a weighed sample is transferred to a shaking bottle. An exactly measured volume of solvent (usually ethyl ether) is added to the sample together with a drying agent (anhydrous sodium sulfate is generally used) and the contents of the bottle are shaken mechanically. Aliquot portions of the resulting oil solution are used for oil determination and for determination of vitamin A by the usual methods.

The freshness of fish is best determined by organoleptic means (that is, by use of the senses such as taste and smell) (20). In order to obtain consistent results, use of a trained tasting panel is advisable. Chemical tests have been devised for this purpose but none is infallible. If a single constituent or group of constituents characteristic of spoiled fish are determined chemically there is no assurance that this particular substance or group of substances actually were formed during spoilage of that particular batch of fish. When fish spoils, a variety of substances may form on different occasions even though storage conditions are substantially identical, so that if chemical means are used as an index of fish spoilage it is usually necessary to determine a number of different spoilage products for each sample examined. Some of the tests that have been successfully used as a measure of fish spoilage include volatile acids, trimethyl-

amine, and volatile reducing substances. Measurement of pH gives little information as to freshness of fish, but is a useful index when applied to oysters.

Table III shows the range of values corresponding to the various conditions of fish freshness for several such tests. In general the determination of total volatile acid has

TABLE III. Freshness Tests for Fish.

Freshness test	Values corresponding to different degrees of freshness			
	Fresh	Incipient decomposition	Stale	Putrid
Trimethylamine, mg. nitrogen per 100 grams fish	0-0.4	0.4-2.0	2.0-4.0	4.0-10.0
Total volatile base, mg. nitrogen per 100 grams fish	4-10	10-15	15-25	25-50
Total volatile acid, ml. 0.01 N acid per 100 grams fish	9-14	14-23	23-50	50-100
Volatile reducing substances, microequivalents per 5 ml. press juice	0-15	15-20	20-30	30-100
pH (for oysters only)	6.1-7.0	5.6-6.1	5.3-5.6	4.6-5.3
Bacterial count, bacteria per gram flesh	0-10 <sup>5</sup>	10 <sup>5</sup> -10 <sup>6</sup>	10 <sup>6</sup> -10 <sup>8</sup>	10 <sup>8</sup> -5 × 10 <sup>10</sup>

found widest application for many species of fish and it is used by some law-enforcement agencies as a legal standard for fish freshness. Trimethylamine has been widely used for nonoily fish such as occur in the North Atlantic area (for example, for haddock and cod). It is not as reliable a test for certain other species such as salmon. Bacterial counts will vary widely depending upon handling conditions, so that values given are merely indicative of counts which are encountered when average commercial handling methods are used. Values for the chemical tests vary somewhat with different species of fish so that the values given are only approximations.

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## FISH-LIVER OILS

Fish-liver oils are valued primarily because they contain vitamin A (see *Vitamins*). The species of fish (*q.v.*) that yield liver oils of greatest value to the North American fishermen are soupfin shark, grayfish (dogfish), halibut, sablefish, lingcod, tuna, and codfish. Ordinarily, the carcasses of soupfin shark and grayfish are discarded at sea, and only the livers are landed. Soupfin shark are difficult to catch, but their livers are large (2-8 lb. in males, 6-16 lb. in females) and contain much oil of a high vitamin A potency (see Table I). Grayfish have smaller livers (0.25-1.75 lb.) that contain oil of

TABLE I. Oil Concentrations and Vitamin A Potencies of Fish Livers.

Fish	Scientific name	Oil in liver, %	Vitamin A per gram oil, U.S.P. units
Male soupfin shark	<i>Galeorhinus zyopterus</i>	50-65	70,000-190,000
Female soupfin shark	<i>Galeorhinus zyopterus</i>	62-78	20,000-45,000
Grayfish	<i>Squalus suckleyi</i>	61-75	3,000-30,000
Halibut	<i>Hypoglossus stenolepis</i>	8-27	42,000-220,000
Sablefish	<i>Anoplopoma fimbria</i>	10-26	65,000-160,000
Lingcod	<i>Ophiodon elongatus</i>	9-20	82,000-500,000
Tuna	—	3-12	14,000-105,000
Cod	<i>Gadus callarias</i> ( <i>G. morrhua</i> )	20-60	1,000-6,000

a lower potency, but these shark are relatively abundant and are taken in large numbers. Other species, such as halibut, sablefish, lingcod, tuna, and codfish, are in demand for food, and their livers are a profitable by-product.

### Vitamin A Relationships in the Fish

Although fish may possibly synthesize vitamin A, many investigators are of the opinion that the vitamin originates from a simple breakdown of the carotenoids present in food consumed by the fish (6).

The liver is the principal organ in which vitamin A is stored, but in certain species, such as halibut and sablefish, vitamin A is also concentrated in the viscera. The larger fish of a given species usually contain livers of a higher vitamin A potency than do the smaller fish, although the variation in potency between individual livers is tremendous. Consequently, this rule applies only to the average of a large number of livers and not to the individual liver. For fish of different species, there is no correlation between the size of the fish and the vitamin A potency of the liver. The dark-colored livers, at least of shark, usually average higher in vitamin A potency than do the light-colored ones. The reverse appears to be true for livers of the seal. Vitamin A appears to be associated with the protein of the liver as well as with the oil, and experiments with grayfish livers have shown that oils of various potencies can be extracted from the liver, depending on the method of rendering. The vitamin A potency of the liver oil of many species shows variations that appear to be associated with the geographical location of the fishing grounds and with the season of the year (2,3,4,9,10).

### Composition of Fish-Liver Oils

**Unsataponifiable Matter.** Fish-liver oils are valued for what would normally be considered impurities in other oils and fats. These impurities constitute the unsaponifiable portion, whose concentration in the liver oil of most food fish is relatively low. For example, in cod, the unsaponifiable portion varies from about 0.1 to 2.4%. Shark-liver oils usually contain a higher proportion of unsaponifiable matter. Grayfish-liver oil contains from about 7.6 to 34.3%, and the liver oils of certain other sharks have been found to contain as much as 81.5% (3).

**Vitamin A<sub>1</sub> and Vitamin A<sub>2</sub>.** The most important constituent in the unsaponifiable matter of fish-liver oil is vitamin A, which occurs as an ester. There are two kinds of vitamin A: A<sub>1</sub> and A<sub>2</sub>. Vitamin A<sub>1</sub> occurs primarily in the liver oil of salt-water fish, whereas vitamin A<sub>2</sub> occurs primarily in the liver oil of fresh-water fish. Vitamin A<sub>2</sub> is important commercially only in so far as it is associated with the vitamin A<sub>1</sub> of salt-water fish. There is no commercial market for vitamin A<sub>2</sub> as such (12).

Vitamin A is, of course, valued because of its function in nutrition. Its property of promoting growth in animals, especially rats, has been used for analysis. Other properties of importance for analytical purposes are the absorption of ultraviolet light and the reaction with antimony trichloride and with glycerol dichlorohydrin to produce blue and purple colors, respectively. Vitamin A<sub>1</sub> absorbs ultraviolet light maximally at 325–328  $m\mu$ . The color produced by the reaction of vitamin A<sub>1</sub> with antimony trichloride dissolved in chloroform absorbs maximally at 620  $m\mu$ , and the color produced by the reaction of vitamin A<sub>1</sub> with glycerol dichlorohydrin absorbs maximally at 550  $m\mu$ . Vitamin A<sub>1</sub> shows a brilliant yellow fluorescence. Vitamin A<sub>2</sub> absorbs max-

imally at 351 m $\mu$ , and the product of its reaction with antimony trichloride absorbs maximally at 693 m $\mu$ . Vitamin A<sub>2</sub> shows a brownish-orange fluorescence (13,14).

**Vitamin D.** Some fish-liver oils are rich in vitamin D. For example, the potency of tuna-liver oils ranges up to 250,000 units per gram; that of swordfish-liver oil up to 25,000 units; that of the group including halibut, lingcod, and rockfish up to 5,000 units; and that of codfish up to 500 units. In contrast to these relatively potent sources of vitamin D are the liver oils of the noncartilaginous fish such as the soupfin shark, whose liver oil seldom exceeds 25 units per gram.

Natural vitamin D, like natural vitamin A, occurs in more than one form, and vitamin D<sub>3</sub> is the one believed to predominate in fish-liver oils. Whereas human beings respond well to either D<sub>2</sub> or D<sub>3</sub>, poultry utilizes D<sub>3</sub> much better than D<sub>2</sub>.

Vitamin D in fish-liver oils was formerly of much greater monetary value than at present. Competition from synthetic vitamin D has lowered the price to such an extent that the vitamin D in fish-liver oil is now of marginal value (4).

**Other Constituents.** The vitamin E or  $\alpha$ -tocopherol found in fish-liver oils is a natural preservative that tends to protect the vitamin A from oxidation. Other constituents in the oil are hydrocarbons, cholesterol, pigments, fatty alcohols, glycerol ethers, and, of course, glyceride fats (15). See also "Marine-oil acids" under *Fatty acids*; and Table II under *Fats and fatty oils*.

#### STABILITY

Vitamin A is decomposed by oxidation or by light. Metals and their salts catalyze the reactions. If oxygen and light are excluded, vitamin A appears to be relatively stable to heat. Most fish-liver oils contain natural antioxidants that give vitamin A some protection against oxidation. The ester form of vitamin A appears to be more stable than the alcohol form (4).

#### Analysis

##### SAMPLING LIVERS

Fish livers have a deceptive appearance in that the relatively small differences in their size, shape, and color do not adequately indicate the tremendous differences in their vitamin A contents, even for livers from the same species of fish. A knowledge of the average vitamin A potency for a given species is of little value for trading purposes, and most livers are bought and sold on the basis of tested potency.

The most reliable method for sampling livers, especially those that are salted, is to pass them through a grinder and into a large vat having an adequate stirring device. The liver material is mixed until uniform, and a sample is then taken. This method, however, is but little used because it has several disadvantages: the grinder and vat are expensive and lack portability; grinding and mixing the livers beat air into them, which may oxidize the vitamin A; and the ground material loses its identity.

The method most widely used employs some type of coring device. The simplest of these consists of a short length of metal tubing that is about 1 in. in diameter and sharpened at one end. The sharpened end is inserted into the liver, and the liver material encased by the pipe constitutes a sample core. This device works only with frozen livers and is laborious to operate. A more elaborate sampler and perhaps the one in greatest use in the U.S. functions on a similar principle, except that the pipe has an auger on the inside. An electric motor rotates the auger, which carries the liver

material up the pipe and into a sample bottle. By using this drill device, the livers can be sampled without first having been frozen (11).

#### ANALYSIS OF FISH LIVERS

A number of different methods are employed for the analysis of fish livers. The ones most commonly used in the U.S. employ some modification of the "shaking method." In this procedure, a weighed quantity of liver is shaken in a bottle with a measured volume of a solvent such as petroleum ether, and the percentage of oil in the liver is calculated from a determination of the weight of oil in an aliquot portion of the solution in the shaking bottle. The oil is recovered from the aliquot portion by evaporating the solvent. The vitamin A potency of the recovered oil is obtained as described below (1).

#### ANALYSIS OF THE FINISHED PRODUCT

The effect of vitamin A on the growth of rats, the reaction of vitamin A with antimony trichloride to produce a blue color, and the absorption of ultraviolet light by vitamin A have all been used for analytical purposes. None of the procedures is completely satisfactory. The rat-growth method lacks precision, requires weeks to complete, and is expensive. Antimony trichloride is corrosive, and the blue color fades rapidly. The absorption of ultraviolet light is quickly and easily measured, but the method lacks specificity. Anything that absorbs light will give a reading, and certain vitamin A oils contain appreciable quantities of such light-absorbing material (7). Morton and Stubbs have developed a correction formula for this extraneous absorption. Thus, the rapid, convenient, and inexpensive ultraviolet-absorption method can now be used with greater assurance that the potencies reported are correct.

The United States Pharmacopeia assay method includes both the Morton-Stubbs and the blue-color methods. The vitamin A potency is calculated from ultraviolet spectrophotometric data that have been corrected by the Morton-Stubbs procedure. However, the ratio of the blue-color potency to the Morton-Stubbs corrected potency must not be less than 1 nor more than 1.3. The same procedure has been adopted as official first action by the Association of Official Agricultural Chemists. In the A.O.A.C. procedure, the amount of vitamin A is reported on a weight basis whereas in the U.S.P. procedure the amount of vitamin A is reported in U.S.P. units. A U.S.P. unit of vitamin A is equal to 0.30  $\gamma$  of vitamin A alcohol or 0.344  $\gamma$  of vitamin A acetate (5).

#### Preservation of Fish Livers

Fish livers are subject to spoilage, which darkens the color of the liver oil, gives it an undesirable odor and taste, and increases its content of free fatty acid. The livers are best preserved by storing them at low temperatures. On shipboard, the livers are usually placed in 5-gal. cans, which are then packed in ice. For longer periods of time, the livers are kept in cold storage at temperatures as low as  $-20^{\circ}\text{F}$ .

If refrigeration is not available, the livers can be preserved by adding 10% by weight of salt or by adding a patented preparation known as Aquacide (16). The salt treatment has been widely used with Mexican shark livers, and Aquacide has been used with codfish livers processed in the maritime provinces of Canada (4,17).

### Liver Processing

**Steaming Cod Livers.** In the steam-processing method, the livers are placed in a large tank into which steam is injected directly. The temperature is brought to 185–192°F., and cooking is continued until the oil is freed from the liver material. In an alternative method, a steam-jacketed kettle is used, and the livers are heated to only 158–167°F. The oil is skimmed off into settling tanks or is passed through centrifugal purifiers to remove suspended solids and moisture. If the oil is to be destearinated, it is cooled slowly to 35°F., and the precipitate is removed by means of a filter press. The liver solids remaining from the first cook are reheated and placed in a hydraulic press. The oil and press cake obtained are suitable for animal feeding. Low (technical) grades of cod-liver oil, called “cod oils,” are generally dark-colored, with a rank odor and high content of free fatty acids; they are used chiefly in leather manufacture.

**Alkali Digestion.** This method of processing can be used with livers of all kinds. The livers are disintegrated by means of a grinder and the resulting mass is pumped into a digestion tank fitted with a mechanical stirring device. One to two per cent by weight of sodium hydroxide or two to five per cent by weight of sodium carbonate is added, and the liver is cooked at 180–190°F. with live steam until the liver tissue has been converted to a liquid state. This usually requires about one hour for grayfish livers that have been passed through a 1/8-in. disintegrator screen and digested at pH 8–9. Any water accumulated from the live steam or used to flush out the liver containers, grinder, and pipes should not exceed one part for each part of liver being digested.

The hot liquor from the digestion tank is passed through a sludger-type centrifuge. To insure complete removal of the oil, the machine is set to skim into the water layer. The effluent oil from the sludger is then passed to a purifier-type centrifuge. (With oily livers, a settling tank can often be used to advantage between the digester and the sludger. The oil that separates out is passed directly to the purifier.) If the resulting oil still contains soap, excess free fatty acid, or moisture, further refining will be necessary. If the oil clouds at a low temperature, it can be cold-cleared by storing it in a cold room and filtering out the precipitate.

In the case of high-potency livers, the water-phase emulsion separated out by the sludger is pumped into a second tank where the emulsion is mixed with a vitamin-poor edible oil, heated to 175°F., and stirred to allow the added oil to extract any vitamin A that may be present. The solvent oil is centrifuged off, and the oil-extraction process is repeated with a second lot of vitamin-poor oil. The process is repeated as often as is justified by the value of the recovered vitamin A. A countercurrent system of extraction may be used to build a low-potency oil up to a higher-potency level. Thus, the solvent oil used in the fourth extraction of one batch of liver material can be used in the third extraction of the next batch, the second extraction of the following batch, and the first extraction of the batch after that. By this means, the potency of the solvent oil can be built up so that it can be sold as a vitamin A oil, and concurrently the amount of vitamin A remaining in the liver material can be reduced almost to zero.

**Other methods of processing** include the cold flotation of cod livers, the steaming of shark livers, pressure extraction, pressure cooking, enzyme digestion, acid digestion, and solvent extraction (3,4,8).

### CONCENTRATION OF VITAMIN A

**Saponification.** In this process, the glycerides in the fish-liver oil are saponified; the products of saponification are dissolved in water; the vitamin A and other un-

saponifiable matter are dissolved by the addition to the mixture of a water-immiscible solvent; the water and solvent layers are separated; and the vitamin A and the rest of the unsaponifiable matter are recovered by evaporating off the solvent. The soap solution is discarded or is used as an inexpensive emulsifier. The solvent is recovered for re-use.

The saponification process is of limited value with oils containing appreciable amounts of unsaponifiable matter. For example, a shark oil containing 20% unsaponifiable matter can be concentrated only fivefold without further isolation of the vitamin A from other unsaponifiable constituents (3).

**Molecular Distillation.** The equipment for the process currently used consists essentially of a heated rotating disk, a pipe to feed oil to the center of it, a trough at its edge to collect the residual oil, and a condenser to collect the volatile constituents. The process is operated in a high vacuum. A number of such stills are used in series, and the residues are subjected to successively higher temperatures as they pass from one still to the next. Thus, constituents of the oil can be separated as follows: (1) any gases contained in the oil; (2) the protein and rancidity odors; (3) the free fatty acids, sterols, vitamin D, glyceride ethers and esters, and such natural preservatives as the tocopherols (vitamin E) and their esters; (4) vitamin A and its esters; and (5) the residue of glyceride fat.

Both vitamin A and vitamin E are recovered as concentrates, but vitamin D is not of sufficient monetary value to warrant separation. The oil residues are sold for food or industrial purposes. The process is particularly useful for those oils containing a high proportion of unsaponifiable matter, such as the liver oil from grayfish (4).

**Solvent Process.** By using propane as a solvent and adjusting the temperature and pressure near its critical point, fish oils can be fractionated to produce concentrates of vitamin A and vitamin D that are 35 times as potent as the original oil. This relatively new process is said to be quick, continuous, and inexpensive. Plants are now in operation in the U.S. and elsewhere utilizing fish-body oils or liver oils (18).

### Economic Aspects

The amounts and values of the various liver oils produced in the U.S. in 1948 are shown in Table II.

TABLE II. Production of Liver and Viscera Oils in the U.S., 1948.

Fish source	Atlantic and Gulf Coasts		Pacific Coast (including Alaska)		Total	
	Gallons	Dollars	Gallons	Dollars	Gallons	Dollars
Cod	214,127	583,426	—	—	214,127	583,426
Shark	"	"	434,010 <sup>a</sup>	6,315,232 <sup>a</sup>	434,010	6,315,232
Tuna	"	"	25,459 <sup>a</sup>	1,094,241 <sup>a</sup>	25,459	1,094,241
Miscellaneous <sup>b</sup>	1,995	111,286	64,546	4,403,467	66,541	4,514,753
<i>Total</i>	216,122	694,712	524,015	11,812,940	740,137	12,507,652

<sup>a</sup> East and West Coast production combined.

<sup>b</sup> Includes the production of burbot-, halibut-, rockfish-, and swordfish-liver oils on the East Coast, and halibut-, lingcod-, sablefish-, and mixed liver oils and viscera oils on the West Coast.

**Foreign Production and Imports.** The principal foreign countries producing fish-liver oils are Argentina, Canada, Iceland, Japan, Mexico, Norway, and the Union of

South Africa. Imports of fish-liver oils and fish livers into the U.S. in 1948 are given in Table III. A comparison of Tables II and III shows that most of the medicinal cod-liver oil used in the U.S. was imported and that the value of imported fish-liver oils exceeded the value of domestically produced oils.

TABLE III. Value of Imported Fish Livers and Fish-Liver Oils, 1948.

Source	Medicinal cod-liver oil, \$	Shark-liver oil, \$	Misc. liver oil, \$	Fish livers, \$	Total value, \$
Canada	757,269	1,777,759	1,105,797	66,099	3,706,924
Argentina	—	2,634,413	—	123,428	2,757,841
Mexico	—	545,617	—	1,417,278	1,962,895
Iceland	1,799,564	—	—	—	1,799,564
Norway	845,449	625,293	53,168	71,177	1,595,087
Japan	110,348	13,557	1,072,220	72,490	1,268,615
Chile	28,686	575,327	—	3,581	607,594
United Kingdom	456,166	—	—	—	456,166
Newfoundland	439,109	—	—	1,616	440,725
Denmark	255,930	—	—	—	255,930
Australia	—	225,472	—	—	225,472
Spain	—	—	165,379	—	165,379
Cuba	—	123,526	—	11,013	134,539
New Zealand	—	111,020	—	—	111,020
Union of South Africa	—	75,110	—	—	75,110
Others <sup>a</sup>	13,872	163,848	109,612	132,451	419,783
<i>Total</i>	4,706,393	6,870,942	2,506,176	1,899,133	15,982,644

<sup>a</sup> Angola, Costa Rica, Portugal, Panama, French Morocco, Canal Zone, Peru, Nicaragua, Uruguay, Sweden, Venezuela, Italy, India, Bahamas, China, Ecuador, Austria, French Guiana, Colombia, Korea, Philippine Republic, Honduras, Brazil, Jamaica.

*Prices.* Fish-liver oil, except that of cod, is priced according to vitamin A potency (see Table IV). Cod-liver oil is still priced by the gallon (in June 1950 the price was listed at \$1.40); this follows a method of sale that dates to a time long before the discovery that the therapeutic value of cod-liver oil is due primarily to its content of vitamins A and D.

Although the price of fish-liver oil has fluctuated widely, none of the price changes has had such a drastic effect on the industry as the decrease that began in 1949 (see Table IV). This decrease, which was attributed to a large influx of imported fish-liver oil and to the greater availability of synthetic vitamin A, caused a number of American fish-liver-oil producers to go out of business.

TABLE IV. U.S. Prices of Fish-Liver Oils<sup>a</sup> of Three Different Potencies.<sup>b</sup>

Year	Price, cents per million units of vitamin A		
	Vitamin A potency of oil in "spectrophotometric" units per gram <sup>c</sup>		
	10,000	100,000	200,000
1946	27-31	32-35	37-41
1947	29-17	35-39	41-43
1948	17-26	34-42	33-43
1949	26-12	38-21	43-24
1950 <sup>d</sup>	12- 6	20- 9	22-15

<sup>a</sup> Excluding cod-liver oil.

<sup>b</sup> At the producer's level.

<sup>c</sup> The *E* value calculated from spectrophotometric data was converted to "spectrophotometric" units using a factor of 2000.

<sup>d</sup> January to June.

### Uses

*Animal Feeds* (see *Feeds, animal*). Although grass, alfalfa, and other materials containing carotenoids furnish much of the vitamin A required by farm animals (the carotenoids are converted to vitamin A *in vivo*), large quantities of low-potency fish-liver oils are used in feeds. Fish-liver oils are also used in pet foods and in the feeding of fur-bearing animals such as foxes and mink.

The oil producers market their products as bulk, unstandardized vitamin A oils, standardized vitamin A oils, and standardized blends of vitamin A and vitamin D oils. The standardized products are also available dispersed in a dry powder.

*Margarine* (*q.v.*) (oleomargarine). Vitamin A is used in the manufacture of margarine, and each pound is fortified to contain 15,000 units. Hence, the fortification of oleomargarine provides a large outlet for fish-liver oils. In order to avoid imparting a foreign taste to the margarine, only the higher-potency oils and concentrates are used for this purpose.

*Pharmaceutical Oils*. In the retail trade, vitamin-A-rich fish-liver oils are available in bottles and capsules. The bottle form is most popular in infant feeding because of ease of administration. Both the bottled and capsuled preparations are available in a wide range of potencies, and the preparations often contain other vitamins; high-potency oils or concentrates are generally favored for capsulation. Fish-liver oils are also available in emulsifiable form, and recent experiments have indicated that vitamin A dispersed in water is more readily absorbed than is vitamin A in the usual oil carriers. Official preparations are: U.S.P. XIV—cod-liver oil (partially destearinated fixed oil obtained from fresh livers of *Gadus morrhua* (L.) and other species of the family Gadidae), oleovitamin A (and capsules), oleovitamin A and D, concentrated oleovitamin A and D (and capsules), non-destearinated cod-liver oil, halibut-liver oil, and halibut-liver oil capsules; N.F. IX—cod-liver oil emulsion, and cod-liver oil emulsion with malt; and N.N.R., 1950—burbot-liver oil, cod-liver oil concentrate (liquid and tablets), cod-liver oil with viosterol, halibut-liver oil with viosterol, percomorph-liver oil, and shark-liver oil.

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**FISH OILS.** See *Drying oils*; *Fats and fatty oils*; "Marine-oil acids" under *Fatty acids*; *Fish*.

**FIXED OILS.** See *Fats and fatty oils*.

**FLAMEPROOFING.** See *Fire-resistant textiles*; *Wood*.

**FLAMES.** See *Explosions (gaseous)*.

## FLAME THROWERS

The flame thrower is a military weapon capable of projecting flaming liquids for considerable distances. It is primarily an antipersonnel weapon, but may be used to burn flammable materials. The flame thrower has great psychological effect, particularly on undisciplined troops. It was used with considerable effectiveness against the Japanese in World War II in certain types of close-range fighting. See also *Gas warfare agents*.

Destructive flammable mixtures of pitch and sulfur were used in warfare by the Greeks as early as 429 B.C. (Siege of Plataea). Greek fire, composed of pitch, sulfur, and naphtha, together with the method of projecting it through brazen tubes or in red-hot balls of iron or stone, were developed by the Greeks in the arsenals of Constantinople and used effectively against the enemy in many of their battles, particularly in the Sieges of Constantinople. The use of Greek fire entirely ceased about the middle of the 14th century. The Prussian Artillery developed and tested a flame projector in 1702, but the idea was soon abandoned. A German engineer, Richard Fiedler, invented a flame projector in 1901, a modified model of which was tested by the German High Command in 1908. This model was improved and a number produced for issue to the troops in 1914. The Germans were the first to use flame projectors in World War I, beginning in the Forest of Malancourt, north of Verdun, on February 26, 1915, and continuing throughout the war for a total of 653 attacks. Flame-projector development by the Allied Nations followed the initial German attack, but their combat use was limited to the French, who first used them on May 21, 1915, in the fighting around Arras, and to the British, who used them in combat late in the war in the Somme and in the Zeebrugge attack, St. George's day, 1918.

All combat nations developed and used flame throwers extensively in World War II in all theaters of operation and on practically all fronts and they were extremely effective. The many types and models were a refinement of those used in World War I.

**Principle of Operation.** Although many types of flame throwers have been developed, the general principles of functioning are the same for all types. A flammable liquid or thickened fuel from a fuel-storage container is forced by compressed gas or a hydraulic pump through a nozzle and then ignited. The propulsion gases of the compressed-gas types of flame throwers may be stored in a separate container under high

pressure (approximately 2000 p.s.i.), or the gases may be generated at the time of use by controlled burning of a powder propellant such as Cordite in a closed system.

The majority of flame throwers are pressurized by compressed gases. The gases used for this purpose include air, nitrogen, carbon dioxide, hydrogen, and combustion gases of gasoline. The gases are stored at a high pressure in order to conserve space and weight. The gas pressure is reduced to a controlled working pressure of 250–500 p.s.i. by means of a conventional automatic regulating valve before it enters the fuel container. The liquid is forced through the nozzle usually by the direct application of the gas at the proper working pressure on the flammable material in the fuel-storage container. Usually the capacity of the high-pressure-gas container is sufficient for only one load of fuel.

Some vehicular-mounted flame throwers are pressurized by a hydraulic pump powered either by a power take-off from the vehicle engine or by means of a separate engine. The power requirement for the hydraulic pump is high (approximately 30 hp. per gallon-per-second discharge) if a direct pressurizing system is used in which the output of the pump is equal to that of the nozzle. The power requirement can be reduced considerably at the expense of increased complexity by means of an accumulator system in which potential energy is stored by compressing a spring or gas cushion over a period of time. Continuous firing, obviously, is not possible with an accumulator system.

Most flame throwers include some type of quick-acting fuel-shut-off valve, usually of the pintle type, to permit controlled intermittent firing. This shut-off valve is hand-operated in portable flame throwers but in large vehicular-mounted flame throwers it frequently is operated by compressed gases.

Nozzles having diameters varying from  $\frac{1}{4}$  in. to more than an inch have been used on flame throwers. Conical nozzles were used on some early models of flame throwers, but most recent models use nozzles having a tapered or rounded approach and a short, straight, cylindrical section. Tests have indicated that range is not markedly influenced by variations of nozzle design, other than the bore diameter.

Various methods of igniting the fuel upon its exit from the nozzle have been used. The fuel of some early models was ignited by a hand grenade or incendiary projectiles after it was projected onto the target area. Some of the early models used a continuously burning wick. A number of models have been designed to use a torch of flammable gas (hydrogen, propane, or acetylene) ignited by an electrically heated hot wire or plate, or by a high-voltage electric spark. The method frequently used in World War II models of vehicular-mounted flame throwers consisted of igniting a spray of atomized gasoline by means of a high-voltage electric spark. The burning gasoline torch enveloped the fuel rod and thereby ignited it. One of the U.S. portable flame throwers is equipped with an incendiary type of ignition which consists of a mechanically actuated pyrotechnic charge that projects a jet of burning particles and gases into intimate contact with the fuel as it leaves the nozzle. Each of several cartridges burns for a few seconds, and can be fired in turn to ignite successive bursts of fuel. The incendiary type of ignition is simple and quite reliable under combat conditions. Most flame-thrower ignition systems are protected by a shield against the adverse effect of winds.

**General Types.** Flame throwers may be divided into two general classes: (1) portable or hand-carried types and (2) large vehicular-transported types. Most of the portable flame throwers weigh less than 80 lb. and are carried by one man. The

fuel unit is usually strapped to the man's back while he carries the flame gun in his hands. A reinforced rubber hose connects the fuel unit with the gun. The fuel capacity of the portable types usually does not exceed 4 gal. and the total duration of fire is generally less than 10 seconds. The maximum range may vary from about 20 yards with unthickened fuels to 60 yards with thickened fuels.

The vehicular-mounted types of flame throwers may be divided into two groups: (1) the large-capacity main-armament types and (2) the smaller auxiliary types. The large-capacity main-armament flame throwers are usually referred to as flame-thrower tanks since they are mounted in tanks and flame throwing is the primary mission of these vehicles. The flame-thrower tanks frequently are equipped with machine guns and a cannon as secondary armament. The main-armament flame throwers usually have a fuel capacity of several hundred gallons and ranges up to 200 yards under favorable wind conditions. Most flame-thrower tanks carry the fuel inside the vehicle; however, during World War II the British used an armored trailer to transport the fuel and pressurizing system. The fuel is connected with the gun on the tank by means of a pipe and flexible coupling. The use of a trailer reduces combat hazards and makes it unnecessary to permanently convert a tank to a flame-throwing vehicle. The heavy trailer reduces the mobility of the tank considerably, but it is possible to jettison the trailer at any time by means of a control inside the tank. The relatively large fuel capacities of main-armament flame throwers make it practicable to use larger nozzle sizes and thereby produce longer ranges. The rate of fuel discharge from the nozzle may vary from 2 to 8 gal. per second depending upon the diameter of the nozzle and the operating pressure.

Auxiliary flame throwers have been developed to provide a supplementary weapon for standard tanks. The fuel capacity may vary from 10 to 80 gal. depending upon the available space in the vehicle. In some models the fuel unit is mounted on the exterior of the vehicle and protected by an armor cover. Due to the limited fuel supply it is necessary to use smaller-diameter nozzles than those used on main-armament flame throwers to conserve the fuel supply. The range of most models varies from 50 to 80 yards, and the rate of fuel discharge is approximately 1 gal. per second.

**Fuels** for flame throwers may vary in consistency from that of gasoline to a semi-solid gel. Thickened fuels, if sufficiently volatile for good ignition, give ranges at least double those attainable with unthickened fuels such as blends of gasoline and fuel oils. The use of thickened fuel permits better firing control, is less affected by adverse winds, and makes it possible to project a greater quantity of fuel on the target than with unthickened fuel. Unthickened fuel burns largely in the air while in flight and is more terrifying and spectacular than thickened fuels but less effective.

Considerable work has been done on developing thickening agents for gasoline. Viscous petroleum products were first used for this purpose. Later, rubber was used with some success. The most successful thickening agents are aluminum soaps (see *Driers and metallic soaps*). The U.S. uses a mixture of aluminum soaps, generally referred to as Napalm, as a thickening agent. A fuel of any desired consistency may be prepared by mixing the proper amount of Napalm with gasoline.

The use of high-consistency Napalm gels at low temperature results in ignition difficulties due to the slow rate of vaporization of the gasoline from the gel. This difficulty is offset in certain main-armament flame throwers by the use of unthickened gasoline as a secondary fuel. About 3% of gasoline is injected into the outer surface of the fuel stream shortly before it enters the nozzle and thus coats the fuel rod with

gasoline, thereby improving ignition. Good ignition is important, not only to ensure that all of the fuel burns but also to obtain maximum range. The range of an unignited jet is less than half that of the same well-ignited jet. The increased range of the ignited jet probably is due to a combination of factors which include decreased resistance of heated air, upward convection currents, and a burning jet effect. Maximum ranges of flame throwers using thickened fuels are obtained at nozzle elevations between 10 and 20°.

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**FLARES.** See *Smokes (chemical) and flares*.

**FLAVIANIC ACID**,  $\text{HOC}_{10}\text{H}_4(\text{NO}_2)_2\text{SO}_3\text{H}$ . See *Naphthols and naphtholsulfonic acids*.

**FLAVICIDIN; FLAVICIN.** See *Penicillin*.

**FLAVIN COENZYMES; FLAVOPROTEINS.** See *Enzymes*, Vol. 5, p. 741; *Fermentation*.

**FLAVONES.** See "Benzopyrans" under *Heterocyclic compounds*.

**FLAVOPURPURIN**,  $\text{HOC}_6\text{H}_3(\text{CO})_2\text{C}_6\text{H}_2(\text{OH})_2$ . See *Anthraquinone derivatives*, Vol. 1, p. 953.

### FLAVORS AND SPICES

*Flavors* are substances used for stimulation of the so-called "chemical" senses, those of taste, mouthfeel, and odor. *Spices* are an aggregation of flavoring agents of plant origin, grown mostly in the tropics, which are characterized by strong pungent odors, biting mouthfeel, and, sometimes, sweet or bitter taste. Simple taste additives are usually called *seasonings*. Complex mixtures of ingredients to be added as the food is eaten are called *condiments*. Those materials added to foods during preparation are called *flavorings*, and individual substances used may conveniently be referred to as *flavorants*, though this term is usually employed only when the substance stimulates both taste and smell. If it stimulates only one of them, it is to be regarded as a seasoning or as an odorant. Thus sugar and salt are not usually called flavorants, but seasonings.

Flavorings for foods, beverages, and medicinals (see also *Pharmaceuticals*) are utilized in various forms: dried plant parts (spices and herbs), either whole or ground; alcoholic extracts; essential oils (see *Oils, essential; Perfumes*), either undiluted, as alcoholic extracts (sometimes called essences), or as emulsions with gum acacia and a heavy sugar or glycerol sirup (see Vol. 3, p. 113); fruit juices, either single strength or concentrated (see Vol. 3, p. 113); synthetic materials. Condiments such as mayonnaise and other salad dressings and vinegar will be discussed in separate articles (see *Salad dressings; Vinegar*).

Standards and specifications for specific flavoring materials are given by the U.S. Food and Drug Administration and also (for medicinal flavors) by the *United States*

*Pharmacopœia* and the *National Formulary*, which give methods of preparation as well. Specific national and state laws apply to foods and to some of their ingredients.

The U.S. Food and Drug Administration has defined spices as "aromatic vegetable substances used for the seasoning of food. They are true to name, and from them no portion of any volatile oil or other flavoring principle has been removed." Spices and herbs usually consist of dried plant parts: leaves (as borage, catnip, chives, dill, fennel, horehound, marjoram, parsley, pineapple mint, rosemary, rue, sage, savory, sweet basil, tarragon, thyme, wintergreen, wormwood); flowers and buds (as cloves, jasmine); fruits (as cardamom, paprika, parsley); seeds, which in most cases are actually fruits (as allspice (pimento), anise, caraway, cardamom seed, celery seed, coriander, cumin, dill, fennel, mustard, nutmeg, pepper, tonka beans, vanilla); bark (as angostura, cassia, cinnamon, slippery elm, wild-cherry bark, witch hazel); roots (as chicory, garlic, gentian root, ginger, horse-radish, licorice, onion, sassafras, turmeric (*curcuma*)); saps, gums (*q.v.*), and other exudations (as gum arabic, gum benzoin, gum tragacanth, honey, manna).

A flavoring extract for food purposes is defined by the Food and Drug Administration as "A solution in ethyl alcohol of proper strength of the sapid and odorous principles derived from an aromatic plant, or parts of the plant, with or without its coloring matter, conforming in name to the plant used in its preparation." Flavoring extracts (variously called fluidextracts, tinctures, or spirits when used in medicinals) are of two main types. One type may be prepared by maceration or percolation of the appropriate plant or plant part with ethyl alcohol of suitable concentration. This is the method usually employed in preparing extracts of vanilla (see p. 589), ginger, and tonka. The second type is usually made by obtaining an essential oil from the plant (root, leaf, fruit, or seed) by distillation or expression and dissolving the oil in ethyl alcohol of suitable concentration. This is the method usually employed in preparing extracts of lemon (see p. 589), almond, anise, cinnamon, clove, nutmeg, rose, and wintergreen. Flavoring extracts of many vegetable substances may be prepared by either of the two methods or by a combination of the two (as in peppermint spirit (U.S.P. XIV) and spearmint spirit (N.F. IX)).

### The Senses Involved in Flavor Detection

The chemical senses are so named because they respond to the presence of chemical substances, which stimulate in ways mostly still unknown. Some theories of sensory stimulation imply that nerves respond to particular types of chemical reaction, such as oxidation, reduction, or the precipitation of protein. Other theories call for receptor cells that respond to electromagnetic waves, particularly those of a certain band in the infrared range. Still other theories envisage physical stimulation of the sensory nerves by electric charge redistribution or some other kind of surface action that takes place in the colloidal dimensions. Indeed, several types of explanation may be required to account for all of the known facts of stimulation, whereby the senses of taste and mouthfeel are activated by substances dissolved in the saliva and the sense of smell by molecules dispersed in the air.

Taste detection is limited to the tongue itself, at the tip, sides, and back. There is an unresponsive area in the center of the top, most prominent in adults. No tasting ordinarily is done by the gums, cheek, palate (roof of the mouth), or throat. There are classically four taste elements: sourness, saltiness, sweetness, and bitterness. **Sourness** is caused by the hydrogen ion, uniquely, and is characteristic of acids and acid-reacting substances such as tannins, alum, phenols, lactones, and some salts and esters. **Saltiness** is caused by the simultaneous presence of monobasic anions and monacid cations, most characteristically in common salt (sodium chloride) but also in a number of other simple salts. **Sweetness** is stimulated by some inorganic ions such as those of lead and beryllium, but more commonly by organic substances containing one or more of several kinds of stimulating

substituents ("glucophores" or "glycophores"), such as amino, amido, hydroxyl, carbonyl, or nitro groups. Bitterness is caused by the same general types of organic glucophores, but usually only when they are replicated or when the molecular weight of the substance is relatively high, for example, 300 or over.

Mouthfeel consists of a group of feeling sensations that are common to the whole body to some extent but are particularly acute in the mucous membranes of the mouth and throat. The sensations of warmth and coolness may be stimulated by a change of temperature, but also by the presence of certain chemical substances, such as ginger, for warmth, and menthol, for coolness. The contact, pressure, or touch component allows us to judge the presence of food and note its fineness, coarseness, greasiness, etc. Astringency is the pucker of the membranes, which are stimulated strongly by alum or tannin. Another important mouthfeel component is pain, caused in desirable degree by mustard, cinnamon, cloves, and pepper. A few substances, including cloves and vanillin, have mild anesthetic action, making the tip of the tongue feel numb as it "goes to sleep." The sensations listed under mouthfeel may also be noted to some extent in the nasal chamber on smelling certain powerful odors. The most conspicuous feeling component in the nasal chamber and the easiest to excite is pain, which characterizes all "pungent" spices and most essential oils.

Odor is detected in the upper part of the nose, voluntarily by sniffing odorized air, and involuntarily by the puff of aroma that is forced up into the nasal chamber from the throat during the act of swallowing. The aromas of some foods, such as freshly brewed coffee, broiled steak, fried clams, doughnuts, or popcorn, come to us under their own power, while those of low-odor foods, such as bread, fats, nuts, and many vegetables and fruits, usually reach the smelling area only by the "back" route, while swallowing.

Odor varies in character according to chemical composition, and some odor experts are able to relate the two, although the relationship is complicated. There are hundreds of thousands of different odors, posing a very considerable problem of description or classification. One method, devised by Crocker and Henderson, seeks to simplify odor description by classification of odors component by component. According to this system, all odors possess some of each of the four postulated components of fragrance, acidity, burntness, and caprylicness ("goatiness"), but in varying degrees. A set of 32 standard substances has been devised to aid in "odor-numbering," with 8 degrees of intensity of each of the four components, abbreviated to F, A, B, and C for convenience. The standard substances, of course, each have all four components, but they are used as intensity standards only for the component designated on the label, the other three components being ignored while the desired component is being concentrated upon. Odor-numbering can be done with all odors of good intensity provided the amounts sniffed (usually about 50 ml. of the scented air) are large enough to smell easily but small enough not to be unpleasantly pungent. Usually, each of the four digits of a number can be found on repetition by the same operator or be duplicated by different operators within a variance of about 1 unit. A few typical odor numbers of flavoring materials are: 6113 for vanillin, 7223 for oil of peppermint, 7733 for citral, 7563 for oil of cloves, 5114 for coumarin, and 8654 for oil of cassia (the number 8654 means 8 out of a possible 8 degrees of F, 6 out of a possible 8 degrees of A, 5 degrees of B, and 4 degrees of C). This method of classification is a considerable departure from the customary methods of odor classification and is therefore controversial. Another and more customary type of classification is that of Billot (2).

### History and Present Status of Flavoring Agents

When cooking was first adopted, it produced new flavors in some of the cooked articles, but more often it resulted in loss of most of the original flavor, making seasoning imperative. Salt had always been eaten to satisfy the craving for this essential mineral, but gradually it came to be used as a corrective for flat-tasting cooked foods and has continued to be so used to this day. Good cooks over the ages had tested all manner of available materials, such as herbs, berries, fruits, and seeds, to find additions to make their cooking more attractive. Smoking and pickling operations were discovered early and applied mostly to improve the keeping of meats, and various kinds of fermentations were developed. These processes incidentally helped develop flavor. When the products of distant lands became available, powerful spices were found to be valuable additions, particularly for masking the effects of partial spoilage, which was all too common in those early unsanitary times, before refrigeration was general. Black pepper, cinnamon, and cloves, in particular, often were valued above their weight in gold, so anxious were cooks to obtain them. It was largely the desire to capture the

long-established and lucrative spice trade that led to the brilliant era of global exploration by Europeans in the 15th and 16th centuries.

In modern times, spices continue to be used as food flavors, supplemented by herbs and essential oils of many kinds and by a host of powerful and useful synthetic substances previously unknown. Today, it is a far cry from salt and the few spices and dried herbs that formerly were used, as much to cover deterioration as for their own flavor, to the rich resources of the present day, most of which are used for flavor alone.

### Nature of Flavoring Agents

The principal components of foods (proteins, carbohydrates, and fats) are relatively low in flavor. Sugar is the only major ingredient with appreciable flavor intensity. It is therefore mostly the "impurities" or trace substances present in foods that furnish the flavor interest. Some foods have good flavor as grown, without treatment, as fruits, nuts, and some vegetables, while others have to have flavor developed by the action of heat in promoting chemical change, as with meats, fish, shellfish, eggs, coffee, peanuts, and chocolate. Heat is thus a potent flavoring agent. Light and air are almost always damaging to flavor, and cold has no effect, provided freezing does not destroy the texture. The action of these physical or environmental factors will not be considered further, however, but only those added materials that contribute flavor to food. Antiseptic and antioxidant actions can also be disregarded, although they are present in limited degree in vinegar and a few spices and in the smoking of meats and fish. Flavor additives can be considered to be without significant preservative value at usual flavor strength and are used only for the effect they have on taste and odor.

Flavoring agents of natural origin may be of the most varied chemical types, including alcohols, ketones, amines, acids, esters, aldehydes, lactones, and occasionally, hydrocarbons or sulfur compounds (in onion, cabbage, etc.), among organic substances, and salts and acids among inorganic ones. Synthetic flavorants may have exactly the same active ingredients as the natural substances they copy, but, in many instances, new flavorants of the same chemical types have been developed that have greater strength and better resistance to aging and processing or produce novel effects. The proportion of flavoring used is generally small, frequently less than a thousandth of a percent in the food as eaten.

Most satisfying flavors are complex, chemically and stimuluswise, stimulating taste, mouthfeel, and odor. Those stimuli for each separate sense, especially for odor, may consist of many ingredients, of several chemical classes. This degree of complexity of flavoring is necessary for fullness or richness of effect. Typically, natural flavors such as those of fruits and spices are fuller and hence more satisfying than the flavors of simple synthetics; however, as time goes on, better and more complicated synthetic mixtures are evolved, often with the admixture of some natural material with the truly synthetic part. Combinations of the two are generally better than purely natural or purely synthetic flavors alone, especially in processed foods.

### Seasonings (Taste Stimuli)

**Sour taste** is provided by acidic substances, such as phosphoric, citric, malic, lactic, tartaric, and acetic acids, as such or as present in fruit juices or vinegar (*q.v.*). In general, small proportions of the stronger acids give quickly disappearing sourness, whereas the larger proportions needed when weaker acids are used produce a more

lasting sourness sensation (see "Acidulants" under *Food chemicals*). Excessive sourness can be made more pleasant and endurable by increasing other taste factors, especially sweetness.

**Saltiness**, for all practical purposes, can be obtained only by the use of sodium chloride (common salt). Other chlorides, such as those of lithium, ammonium, and potassium, while salty, are too toxic for food use, and the last two are somewhat bitter besides.

**Sweetness** is normally obtained by the use of sucrose, in the form of cane sugar or beet sugar or that present in fruits. Invert sugar has about the same sweetening power as sucrose, is present in honey, and is often used in confections. Dextrose (*q.v.*) or corn sugar is about 60% as sweet as sucrose and, while possibly more expensive on the sweetness basis, may be economical for texture and body in candy, preserves, and sauces, especially when only moderate sweetness is desired. Milk sugar (lactose) is the natural sweetening agent in milk but is too expensive for use as an added sweetener in other foods. Fructose (levulose) is somewhat sweeter than sucrose, on the weight basis. It is a component of invert sugar and is present in certain sweetening sirups made from corn and other vegetable sources. All of the common sugars are proper to use in sweetening foods, and all have about equal nutritive value (see also *Sugars*).

Glycerol also has considerable sweetness but is too expensive to use as a sweetener, except in some medicinals. Of the synthetic sweetening agents (*q.v.*), which have no food value in themselves, certain ones such as saccharin and cyclamate sodium (sodium cyclohexylsulfamate, Sucaryl sodium),  $C_6H_{11}NHSO_3Na$ , are not toxic and are usable in medicines and in foods for diabetics. Cyclamate withstands cooking in foods. Others such as dulcin (sucrol, 4-ethoxyphenylurea, *p*-phenetylcarbamide) and P-4000 ("Verkade's compound," 2-amino-4-nitro-1-*n*-propoxybenzene, 5-nitro-2-*n*-propoxyaniline; see Vol. 1, p. 929) are toxic substances, in the opinion of the Food and Drug Administration.

**Bitterness** is inherent in foods containing natural tannins, alkaloids, and glycosides of many types. Most flavoring is concerned with covering excessive bitterness rather than in adding to it. Covering is best done by adding sourness, sweetness, and saltiness. The addition of aromatics may then provide further interest. Where added bitterness is desired, it may be secured with caffeine, licorice, cocoa powder, chocolate, coffee, tea, hops, gentian root, and many other herb or vegetable products or their extracts, or by use of proprietary "bitters."

**Mixed taste stimuli** are not common. One of the most important seasonings in this class is *monosodium glutamate* (*M.S.G.*),  $NaOOCCH_2CH_2CH(NH_2)COOH$ , white soluble crystals (see also Vol. 1, p. 724), which adds a good balance of sweetness, saltiness, and bitterness to foods (5,11). Its use in amounts in the 0.05-0.25% range in cooked foods does not greatly disturb the seasoning balance but adds materially to the total taste level. It is particularly effective as an intensifier of the flavor of meat products.

Seasonings keep indefinitely on storage and are resistant to processing of the foods.

### Condiments and Flavorings (Mouthfeel Stimuli)

The spices ginger and cardamom provide strong stimulation of the **warmth** factor of mouthfeel. There is a great deal of confusion between true warmth and pain as feeling factors, so that these two sensations can well be considered together. The



sensation of **pain**, to the degree called "bite," or sometimes the lower degree called "warmth," is stimulated by many of the spices, particularly by nonvolatile components of red, black, and white peppers and ginger, and the volatile oils of mustard, cloves, cinnamon, and cassia (see p. 588). Certain herbs or vegetables, such as horseradish, onion, and garlic, also are powerful stimuli of the pain factor.

Menthol (*q.v.*), isolated from the Japanese type of peppermint oil, and most peppermint oils as such possess **coolness**-stimulating action in high degree, on the skin and on mucous membrane. On sniffing these substances, coolness may be felt in the nasal chamber, together with irritation if the quantity is considerable. On the tongue, these substances produce only coolness, with or without some bitterness of taste. A synthetic compound, 3,3,5-trimethylcyclohexanol (Cyclonol), stimulates coolness feeling in shaving preparations, lotions, and other preparations used externally.

**Astringency** is conveniently added by means of the natural tannins present in tea, kola (cola), cassina, and oakwood extracts. (Oak flavoring is important in whiskey and most other distilled liquors.)

A few of the most-used condiments may be noted. *Soy sauce* is a neutralized product of the acid hydrolysis of soybean protein. It is a liquid that is high in salt, glutamate, and brown color, and it is much used as a condiment in the Far East. It is an ingredient of all Worcestershire-type sauces for meat. *Curries* are East Indian condiments, used on rice and other bland foods. They are made from curry leaves, garlic, ginger, pepper, and other spices, including turmeric for coloring; cumin is often included. *Chili powder* is composed of dried chilies, onion, cumin, and oregano. *Prepared mustard* is a paste made from ground mustard seed, flour, or cake. It is widely used on meats, eggs, and cheese.

### Spices and Strong Herbs (Odor Stimuli)

Odor stimuli are so numerous that it is desirable to treat them in at least two groups. For present purposes, they will be divided into spices and strong herbs as the first group, and fruits, vanilla, and miscellaneous as the second. The first group is mostly of natural origin and the second largely synthetic, but both groups are somewhat mixed in this respect.

With spices and strong herbs, the natural substance may be used, whole or ground, to add the aromatic element to foods, beverages, and medicines. These substances give distinctive and interesting flavors and may be grouped by the aromatic components (see Table I). Sometimes they will disperse completely, but at other times they may remain in "hot spots" scattered throughout the food. They may introduce molds and bacteria into foods and cause spoilage unless the food is well cooked, although cloves is actively antiseptic. Further, spices tend to be variable in intensity from lot to lot, due to adulteration or to different lengths of storage before use and, in the cases of paprika, red pepper, and a few other spices, to insect attack (9).

To overcome these variations and troubles, many spice dealers furnish either sterilized spices of calibrated strength or spice extracts which are sterile. Most of these extracts fall considerably short of the full flavor of the spice, especially when the extraction is only partial, but they are convenient to use, usually are uniform from lot to lot, and are sterile. Essential oils of the spices are sterile and provide most of the aroma of the spices, but they may be short in taste and feeling factors. Imitation or reconstituted spices also have been produced, using powdered substances such as nut-

TABLE I. Flavor Characteristics of Spices and Herbs.

Group 1. Flavors Principally in their Essential Oils.		
(Used in all kinds of foods, beverages, and medicinals.)		
Allspice	Celery seed	Fennel
Angelica root (or seed)	Cinnamon	Laurel leaves (bay)
Anise	Cloves	Mace
Caraway	Coriander	Nutmeg
Cardamom	Cumin	Parsley
Cassia	Dillseed	Star anise
Group 2. Flavors in Essential Oils, Plus Bitter Principle.		
(Used in all kinds of foods, beverages, and medicinals, where bitterness is permissible. Particularly valuable in sausages and meat stuffings.)		
Marjoram	Rosemary	Sweet basil
Mint	Sage	Thyme
Origanum (oregano)	Savory	
Group 3. Prominent Biting Principles.		
Capsicums (red pepper, cayenne, chilies, paprika) . . . hot and astringent oleoresins, containing capsaicin		
Garlic . . . powerful sulfury fragrance and moderate bite		
Ginger . . . warm-feeling due to "oleoresin"		
Mustard . . . bite due to allyl isothiocyanate		
Onion . . . biting and sulfury when raw; mild when cooked		
Pepper: black . . . hot and biting due to piperin, and also aromatic		
white . . . decorticated black pepper		
Turmeric . . . gingery taste, but used mostly for its color		
Group 4. Nonvolatile Extractives.		
Fenugreek . . . maple-like, water-soluble		
Tonka . . . coumarin-rich aromatic		
Vanilla . . . vanillin-rich aromatic		
Group 5. Mild Oily Flavors.		
(Used mostly as dressing on outsides of cakes and candies.)		
Flaxseed	Poppy seed	Sesame seed

shell powder, toasted cereals, salt, or sugar flavored with synthetic substances or with the extracts of actual spices.

Spices have been described in detail by Parry (10). Natural spice may be analyzed for strength and for freedom from adulteration by the methods of the Association of Official Agricultural Chemists (A.O.A.C.), Section 33 (1). Section 25 of this book applies to flavoring extracts.

A method was devised by Cartwright and Nanz, in 1948, for strength and quality evaluation of spices, herbs, and other flavor adjuncts. The flavorants are used in several different types of relatively bland test foods such as cream sauce, sugar sirup, eggnog, pumpkin, a cabbage relish, and chopped meats, raw and cooked. This method is well suited for taste panel operation but can also be used by individual testers. Methods of evaluating foods for flavor factors by trained individuals are usually called "organoleptic techniques" (3) (see also *Food and food processing; Food analysis*).

All spices and most herbs are aromatic or odoriferous, and many of them are strongly so. Many also are taste or feeling stimuli. Coolness is distinctive of peppermint. Sweet tastes are conspicuous in anise, cassia, cinnamon, fennel, juniper berries, paprika, star anise, tarragon, valerian root, and wintergreen. Bitter tastes are conspicuous in basil, celery, fenugreek, gentian root, juniper berries, laurel leaves, marjoram, nutmeg, origanum, rosemary, sage, savory, spearmint, thyme, and turmeric. Warmth is found in allspice, basil, cassia, cassia buds, caraway, cardamom, celery, cinnamon, cumin, dill, ginger, mace, mint, nutmeg, origanum, pepper (black and white), sage, savory, thyme, and turmeric. Sting, bite, pungency, or astringency characterize angelica, basil, capsicum, caraway, cassia, cinnamon, cloves, dill, garlic, ginger, laurel (bay) leaves, mustard, nutmeg, onions, peppers of all kinds, rosemary, sage, sassafras, savory, and zedoary.

A few of the natural products listed under spices have considerable coloring power, which is the principal reason for their use. Turmeric (curcuma) is an example (see Vol. 5, p. 352). This has a bitter peppery taste and a weak aroma. Its yellow or orange-yellow color is useful in coloring curries, mustard, and pickles. Paprika is a sweet red pepper, rich in vitamins A and C, not at all "hot," which is useful for producing an orange-red color when the powdered material is used as a garnish for cooked fish, cheese dishes, and the like. True saffron is used occasionally for its orange color, especially in soups.

Spice flavoring is particularly useful in meat products such as sausages and bologna, the distinctive flavors of which are traditional. Frankfurters without lots of salt and pepper would not be recognizable. Mustard is a favorite seasoning for meats. Poultry stuffings require sage, marjoram, and savory. Pickles and relishes use spices freely and in various combinations. Swedish pastry requires cardamom flavoring, and breads may be flavored with caraway, cinnamon, dill, or poppy seeds. Cakes and cookies often contain anise, cinnamon, coriander, or cloves, and apple pies are made more interesting with allspice, cinnamon, nutmeg, or mixtures of these spices. The flavors traditional in Christmas candies include anise, cinnamon, cloves, peppermint, sassafras, and wintergreen. The spices cinnamon and cassia are somewhat interchangeable, having cinnamaldehyde as their chief flavorant, and barky undertones; Europeans largely use the "softer" cinnamon, whereas Americans use the "harsher" cassia.

### Odor Stimuli Other Than Spices

#### FRUITS

Fresh fruits, picked at the peak of ripeness, have delightful flavor, which includes sweetness, more or less tartness and astringency of taste, and aroma. It is the aroma that is distinctive. It usually is very delicate, remaining at optimum character and attractiveness only for a matter of days. On cooking, nearly every fruit flavor is changed in character, producing virtually new flavors, which may be well liked but which do not have the liveliness of the fresh fruit flavor. Partial exceptions are the raspberry and, to a lesser degree, the blackberry, which retain enough aroma character in the cooked form not only to be recognizable but often to be useful in supplying fruitiness, in candies and pastries, to strawberries, blueberries, and other fruits that have lost most of their own.

A technique recently applied to apple juice and to a few other juices strips off the

delicate aroma rapidly by distillation, and concentrates it manyfold. This very volatile flavor, called a "volatile fruit concentrate," is true in character and, if not heated with acid juices, has good lasting power.

The skins of citrus fruits, including oranges, lemons, and limes, contain little round cells of oil at the very outside. While in these cells, the oils are protected against oxidation but, when squeezed out and collected, are prone to develop "terpiness" of flavor, due to oxidation of the 90–95% content of dipentene and other terpenes. If the terpenes are largely removed, by solvent extraction or vacuum distillation, a more stable concentrated oil is obtained, though at the sacrifice of strength and character. In food products (other than beverages) that are not heated enough during preparation to drive off the terpenes, it is best to use terpeneless oils in whole or in part.

The lemon oil expressed from the fresh peel may be dissolved in ethyl alcohol of the proper strength to form lemon extract. The Food and Drug Administration standards state that lemon extract "contains not less than 5% by volume of oil of lemon." The standards for the "terpeneless extract of lemon" state: "It contains not less than 0.2% by weight of citral derived from oil of lemon."

Many excellent fruit flavors have been made synthetically and are specialties of the various flavor houses. These synthetic flavors often contain esters (such as butyrates) and aldehydes similar to those present in the actual fruits but generally selected for greater stability. Occasionally, new compounds are used that are not found in nature. The best fruit flavorings usually are composed of true fruit in concentrated form with a mere trace of synthetic flavorant, to complete and enliven the aroma.

#### VANILLA

Probably the most important single flavorant is vanilla, which may be used alone or in combination with chocolate (*q.v.*) and many other flavors. The vanilla "bean" (the fruit of a vine, *Vanilla planifolia*) contains several flavoring substances, developed from an insipid banana-like pod by enzymic action during the process of curing. One of these substances is vanillin (4-hydroxy-3-methoxybenzaldehyde, vanillaldehyde),  $\text{CH}_3\text{O}(\text{OH})\text{C}_6\text{H}_3\text{CHO}$  (see *Phenolic aldehydes*), present to the extent of 1.5–3.0% in the cured "bean," along with some 10% of other extractives. While vanillin is the most powerful flavorant, the other substances present modify it with rich balsamic character.

Vanilla may be used as such, in comminuted form, as is characteristic of the "Philadelphia" type of ice cream, or vanilla flavoring may be imparted to sauces or liquids by the whole bean suspended in them by a string. A new process of curing vanilla produces a powder, which can be used directly for flavoring but is best used for making extracts. Most vanilla flavoring is done with extracts or with dry or moist vanilla sugar, made from extract taken up with sugar.

Vanilla tincture, according to the U.S.P. XIV, is made by maceration of vanilla beans with water, ethyl alcohol, and sugar for a period of 3 days, followed by careful percolation. A liter of finished tincture contains 380–420 ml. of ethyl alcohol, 200 grams of sugar, and the extractables of 100 grams of vanilla. All vanilla *extracts* are so made, but in recent years the high tax on alcohol has caused some firms to substitute propylene glycol for the alcohol, to produce vanilla "flavoring," in order to meet competitive prices. While propylene glycol is permissible in such products,

much (even of the "pharmaceutical grade") of this substitute introduces a disagreeable aftertaste that is distinctly noticeable even with the small quantity added as vanilla flavoring. Also, propylene glycol fails to extract all of the delicate flavor. The best vanilla, the true *extract*, is that containing no propylene glycol.

Vanilla may be reinforced in strength with synthetic vanillin, up to a certain point, without too much damage being done to flavor quality. It must be remembered, however, that true vanilla extract, while equivalent to 0.7% vanillin in strength, contains only 0.15–0.30% vanillin, and that doubling the total strength by adding up to 0.7% vanillin may be as much as is desirable, qualitywise. Many vanilla imitations are on the market; the best contain vanillin, ethyl vanillin, or a very little coumarin, with or without some true vanilla, and the poorest contain coumarin in larger amount. Coumarin is a flavorant in its own right and may be liked as such, but it tends to dominate in vanilla.

#### MISCELLANEOUS

The essential oils of anise, bitter almonds, peppermint, sassafras, spearmint, and wintergreen provide good flavor cheaply for candies, jellies, toothpastes, etc., and all of these are more or less resistant to oxidation. Other stable oils that are useful in traces for special flavoring effects include angelica (celery-like), neroli (orange blossom), otto (attar) of rose, and patchouli (musty mintiness) (see also *Oils, essential*). Flavor effects may be extended by adding many of the specialties of the flavor houses, including fruits and traces of  $\beta$ -ionone. The many so-called "aldehydes" and some true aldehydes available are extremely potent but if used carefully are valuable in fine flavors ("aldehyde" has come to mean nearly any powerful flavorant). The use of synthetics and the creation of imitation flavors has been described in great detail by Jacobs (7).

Citrus oils, as such, find wide use in carbonated beverages (*q.v.*), including orange drinks, rickies, the cola beverages, and ginger ale. For this usage, the terpeneless oils are generally inferior to the complete oils, and must not replace them in entirety. "Oil of limes, distilled," a favorite beverage ingredient, has a flavor character produced by the distillation process that is not found in "oil of limes, expressed." Sometimes synthetic cinnamaldehyde is used in place of oil of cassia, in beverages, as in foods and medicines, to give cinnamon character, but it should not entirely replace the natural oil, which has much richer flavor. Benzaldehyde finds application in cherry drinks, as such, or in "wild-cherry" extracts and in almond extract for cake icings. Ginger ale cannot be made solely with oil of ginger, which has no appreciable warmth and contains so much terpene that it may cause excessive belching. Only a ginger extract can furnish the warmth. The ginger flavor is finest when the extract is made from fresh ginger root, but can be good when made from "oleoresin" ginger and ginger oil.

Among dairy products (*q.v.*), butter and certain cheeses contain the volatile but powerful aromatic ketone, biacetyl (diacetyl),  $\text{CH}_3\text{COCOCH}_3$ , as well as traces of butyric acid and butyrates. All of the synthetic flavorings used in making butter-scotch candy, sauce, etc., and some other apparently unrelated flavors depend upon these and similar substances. Biacetyl has a most powerful odor, burnt and irritating, but it is extremely useful in high dilution. Many other strong or even unpleasant substances, such as the sulfur compounds of garlic and onions, can be most valuable when used in similarly controlled traces.

Economic Aspects

The figures in Tables II and III were taken mostly from the U.S. Department of Commerce, Office of International Trade (*World Trade in Commodities Supplement*, Vol. VII, Parts 6, 7, and 8, Supplement No. 11, March, 1949). The net imports of most spices and herbs correspond with consumption, but notable exceptions are mustard,

TABLE II. Spice Imports and Prices of the More Important Items.

Item	Condition	Imports, 1,000 lb.		Price, av., \$/lb.	
		1935-39 av.	1948	1935-39	1948
Allspice (see "Pimento")					
Anise seed.....	Whole	533	1,139	—	—
Caraway seed.....	Whole	6,047	4,367	—	—
Cardamom seed.....	Whole	216	143	—	—
Capsicum (red cayenne, pepper, and chili).....	Unground	1,501	3,170	0.079	0.219
Cassia and buds.....	Unground	10,169	6,900	0.077	0.156
Celery seed.....	Whole	1,291	2,065	—	—
Cinnamon and clips.....	Unground	277	66	0.123	0.303
Cloves.....	Unground	5,030	6,066	0.123	0.074
Coriander seed.....	Whole	2,162	2,165	—	—
Cumin seed.....	Whole	938	2,860	—	—
Curry and curry powder...	Ground	38	9	—	—
Fennel seed.....	Whole	272	194	—	—
Fenugreek seed.....	Whole	544	1,473	—	—
Ginger root (not candied or preserved).....	Unground	2,509	3,436	—	—
Laurel leaves.....	Bulk or bales	—	339	—	—
Mace.....	Unground	781	561	0.393	1.01
Marjoram leaves.....	Unground	67	—	—	—
Mixed spices.....	Ground	583	938	—	—
Mustard seed.....	Whole	11,039	9,990	0.044	0.114
	Ground or prepared	1,055	228	—	—
Nutmegs.....	Unground	4,405	4,810	0.112	0.380
Origanum.....	—	—	626	—	—
Paprika.....	—	6,337	6,404	0.139	0.293
Pepper:					
Black.....	Unground	50,086	27,174	0.047	0.440
Red (see "Capsicum")					
White.....	Unground	6,444	2,563	0.091	0.580
Pimento (allspice).....	Unground	2,145	1,895	—	—
Poppy seed.....	Whole	7,673	6,071	—	—
Saffron.....	Crude	4	6	—	—
Sage.....	Unground	1,653	1,454	—	—
Thyme leaves.....	Unground	100	1	—	—
Tonka beans.....	—	625	504	—	—
Turmeric (curcuma).....	—	1,066	1,382	—	—
Vanilla beans.....	—	127,158	101,669	2.50	4.77

paprika, and capsicum, a great deal of which is grown in the U.S. U.S. production of mustard averaged 25,550,000 lb. per year for the 1935-44 period and was 46,940,000 lb. in 1946. The postwar year 1948 is compared with the five-year prewar average, 1935-39, in Table II.

Import and U.S. production figures for essential oils (*q.v.*) important in flavoring are given in Table III.

TABLE III. Imports and U.S. Production of Essential Oils of Flavor Interest.

Oil	Imports			
	Amount, lb.		Price, \$/lb.	
	1937	1947	1937	1947
Anise.....	293,000	441,000	0.62	0.73
Cassia.....	250,000	137,000	0.66	1.98
Clove.....	38,000	113,000	0.67	0.69
Cinnamon bark.....	233,000	352	0.83	42.50
Cinnamon leaf.....	—	11,200	—	5.08
Lemon.....	89,000	52,000	2.63	2.73
Lemon, terpeneless.....	—	156	—	36.90
Lime.....	118,000	108,000	5.16	4.28
Orange.....	205,000	89,000	1.23	1.44
Orange, terpeneless.....	—	18	—	163.00
Peppermint.....	1,005	11,200	6.60	2.63
Rose otto.....	2,400	1,785	111.50	448.00

	U.S. Production			
	Amount, lb.		Price, \$/lb.	
	1936-45 av.	1947	1936-45 av.	1947
Birch (sweet).....	—	10,000	—	—
Grapefruit.....	—	50,000	—	—
Lemon.....	—	1,000,000 <sup>a</sup>	—	—
Orange.....	—	750,000 <sup>a</sup>	—	—
Peppermint.....	1,056,000	1,603,000	3.73	6.74
Sassafras.....	—	25,000	—	—
Spearmint.....	189,000	481,000	2.38	5.57

<sup>a</sup> Approximate.

Table IV gives figures for U.S. production and sales of flavor and perfume (*q.v.*) materials for the year 1948, compiled by the Chemical Division of the U.S. Tariff Commission, June 1949. No separation was made between those substances used only in perfumes and those used in both perfumes and flavors.

TABLE IV. U.S. Production and Sales of Flavor and Perfume Materials, 1948.<sup>a</sup>

Material	Production, 1,000 lb.	Quantity, 1,000 lb.	Sales	
			Value, \$1,000	Unit value, \$/lb.
Grand total.....	22,192.5	19,016.5	26,710.2	1.40
CYCLIC				
Total.....	15,414.5	12,535.8	16,713.4	1.33
Benzenoid and Naphthalenoid				
Total.....	9,091.9	8,175.9	8,984.4	1.10
Acetophenone.....	57.2	58.7	77.8	1.33
$\alpha$ -Amylcinnamaldehyde.....	115.6	89.4	187.4	2.10
Anisaldehyde.....	132.8	129.8	255.5	1.97

TABLE-IV. U.S. Production and Sales of Flavor and Perfume Materials, 1948<sup>a</sup> (Concluded).

Material	Production, 1,000 lb.	Sales		
		Quantity, 1,000 lb.	Value, \$1,000	Unit value \$/lb.
Benzenoid and Naphthalenoid (Continued)				
Benzophenone.....	77.3	71.3	85.2	1.19
Benzyl alcohol <sup>b</sup> .....	605.4	556.5	276.3	0.50
Cinnamic acid.....	30.0	—	—	—
Eugenol.....	61.1	56.5	164.4	2.91
Isoeugenol.....	40.1	—	—	—
<i>p</i> -Methylacetophenone (methyl <i>p</i> -tolyl ketone)...	17.1	16.7	17.3	1.04
Methyl eugenyl ether (methyleugenol).....	0.7	0.5	2.4	4.80
Musk xylene.....	140.1	146.1	220.3	1.51
Phenethyl alcohol ( $\beta$ -phenylethyl alcohol).....	404.0	287.8	378.7	1.32
3-Phenyl-1-propyl alcohol (hydrocinnamyl alcohol).....	8.7	—	—	—
Vanillin.....	932.4	793.2	2,190.7	2.76
All other benzenoid and naphthalenoid compounds <sup>c</sup> .....	2,507.6	2,225.1	3,520.9	1.58
Terpenoid, Heterocyclic, and Alicyclic				
<i>Total</i> .....	6,352.6	4,359.9	7,729.0	1.77
Cedrol.....	5.9	5.7	6.9	1.21
Citral.....	32.1	30.5	106.8	3.50
Citronellol.....	89.1	47.6	125.8	2.64
Coumarin, synthetic.....	456.9	396.9	1,039.4	2.62
Geraniol.....	229.0	114.1	233.5	2.05
Hydroxycitronellal.....	66.0	35.7	229.0	6.41
Indole.....	—	4.2	63.8	15.19
$\alpha$ -Ionone.....	9.0	4.3	30.7	7.14
$\beta$ -Ionone.....	12.0	—	—	—
Ionone, all other.....	42.0	41.4	144.0	3.48
Linalool, natural.....	37.9	23.6	106.4	4.51
Menthol, synthetic, tech.....	131.9	114.6	484.5	4.23
Methylionone.....	102.6	83.0	363.3	4.38
Nerol.....	1.5	1.6	12.0	7.50
Piperonal (heliotropin).....	128.8	—	—	—
Rhodinol.....	4.3	4.1	124.9	30.46
Safrole.....	143.2	112.7	84.1	0.75
All other terpenoid, heterocyclic, and alicyclic materials <sup>c</sup> .....	4,607.2	3,138.9	4,289.0	1.37
ACYCLIC				
<i>Total</i> .....	6,748.0	6,480.7	9,996.8	1.54
Glutamic acid, monosodium salt (monosodium glutamate).....	6,158.7	6,070.6	9,387.7	1.55
Methylheptenone.....	1.7	1.5	7.4	4.93
<i>n</i> -Octyl aldehyde (C <sub>8</sub> ).....	0.9	—	—	—
Undecylenic acid.....	127.4	30.9	44.5	1.44
All other acyclic materials <sup>c,d</sup> .....	284.9	197.4	402.6	2.04

<sup>a</sup> The 1948 values for organic esters that appear on pp. 839-40 of Vol. 5 have not been repeated in this table, but they are included in the totals.

<sup>b</sup> Includes minor quantities of technical benzyl alcohol.

<sup>c</sup> Does not include those organic esters reported on pp. 839-40 of Vol. 5.

<sup>d</sup> Includes data on production and sales of chemically modified essential oils.



The preliminary report for 1949 indicates that the U.S. production of synthetic menthol was almost doubled, increasing from 131,900 lb. in 1948 to 253,900 lb. in 1949, despite continuing imports from China and Brazil of natural menthol, obtained from peppermint oils. The production of safrole, the main constituent of sassafras oil, also increased considerably, from 143,200 lb. in 1948 to 272,400 lb. in 1949. The production of both vanillin and coumarin did not come up to the 1948 output. This might be explained in part by the carry-over of ample stocks from the previous year. The unit value of vanillin was reduced from \$2.76/lb. to \$2.64, while that of coumarin remained unchanged. The production of monosodium glutamate, which is produced in larger quantities than any other flavor material, increased from 6,158,700 lb. in 1948 to 7,642,500 lb. in 1949.

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**FLAX.** See *Linen*.

**FLAXSEED OIL.** See "Linseed oil" under *Drying oils*; *Fats and fatty oils*.

**FLINT.** See *Abrasives*, Vol. **1**, p. 4; *Ceramics (whiteware)*; *Glass*; *Silica and silicates*.

## FLOTATION

Flotation is a method of materials separation developed for the concentration of metallic minerals and based on the affinity of properly prepared mineral surfaces for air bubbles. In froth flotation (by far the most usual form) a froth is formed by introducing air into a pulp of the finely divided ore and water containing a frothing agent. Those minerals that have an affinity for air bubbles rise to the surface in the froth and are thus removed from those that are completely wetted (see Figs. 2 and 4). The field of flotation application has been extended to include the recovery of almost all minerals from the ores in which they occur, as well as the separation of many solid and liquid substances in the field of chemical engineering. Its most general use is as one of the steps in the present production of almost all copper, lead, zinc, nickel, and silver. Its chief advantage is relatively efficient operation at substantially lower cost than many other processes formerly employed.

Separations made by flotation include not only the concentration of base-metal ores but also widely divergent applications such as the separation of ink from repulped paper stock, of peas from pea pods, of oils from industrial wastes, of coal from slate, and of potassium chloride from sodium chloride. The first and most thoroughly studied application, however, is in the field of mineral engineering, and, therefore, it is appropriate to consider the subject from this aspect.

Flotation as applied to the concentration of minerals, is used in conjunction with other mineral engineering operations such as comminution, classification, gravity concentration, thickening, and filtration (see *Filtration*; *Gravity concentration*; *Sedimentation*; *Size reduction*; *Size separation*). In general, crude ores from the earth are crushed, ground in ball mills in the presence of water, classified in water, and then treated by flotation to produce a concentrate of one or more minerals, while the remainder of the minerals of the ore remain behind in the water pulp. The concentrate is thickened, filtered, and then sent on to whatever chemical or pyrometallurgical treatment may be required to prepare it for ultimate consumer use. Flotation is such a versatile tool that any, all, or none of the above mentioned auxiliary operations may be used in conjunction with it. The production and control of surface films require the extensive use of organic, inorganic, and colloidal chemistry, so that the subject is of great complexity. However, most of the practice of flotation is still empirical and the fundamental principles are the subject of much debate and disagreement.

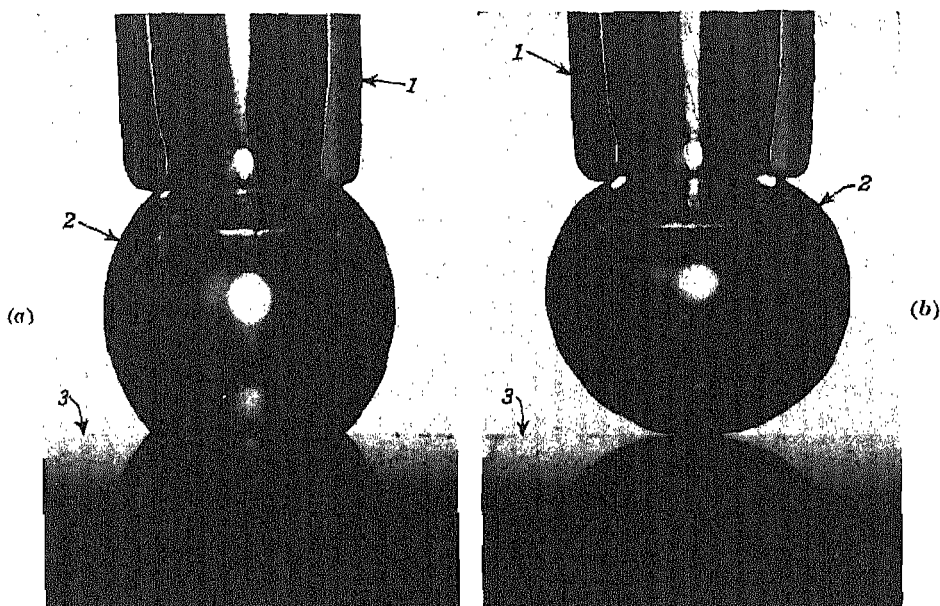
### Theory

In principle, flotation depends on the relative wettability of surfaces. A flotation system consists of a liquid, a gas, and some particulate material. The particulate material may be a liquid, such as oil droplets, but it usually is a solid ranging in size from somewhat less than 1 mm. to finer than 1  $\mu$ . The surface of the material may exhibit a natural nonwettability, but it usually must be treated with various flotation reagents in order to produce the desired degree of wettability or nonwettability. See *Surface properties*.

Flotation theory may be presented by considering separately the chemical and the physical factors involved. The characteristic feature of flotation, as distinct from other methods of mineral concentration, is that the separation is made on the basis of the relative wettability of mineral surfaces (5). The major technical problems are those concerned with the chemical control of mineral surfaces.

**Chemical factors** to be considered in flotation include the crystal structure of minerals, the structure and composition of water, the chemistry of flotation reagents and their surface chemical reactions with minerals, and the natural associations of minerals.

Most minerals exhibit a strongly polar surface and thus are wetted by water, provided that the surface is not contaminated with a nonpolar substance such as a grease. Exceptions are talc,  $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ , and pyrophyllite,  $\text{H}_2\text{Al}_2(\text{SiO}_3)_4$ , in which the nonpolar bonds are buried within double sheets of linked tetrahedra represented as  $\text{Si}_4\text{O}_{10}$  (1). The cleavage of these minerals therefore exposes surfaces which have no unsaturated bonds and hence will not attach to the hydrogen or hydroxyl ions of water.



1. Bubble holder 2. Air bubble 3. Mineral surface

Fig. 1. Air bubble on a clean galena surface in (a) water and (b) a solution containing 25 p.p.m. potassium ethyl xanthate ( $\times 15$ ).

This failure to attach to water means that the minerals will preferentially attach to air; thus, talc and pyrophyllite may be classed as "natural floaters." However, this classification is not accepted by all authorities in the field.

The ionization (and polarity) of water in addition to its ready availability make it the most useful liquid for flotation. The conditions required for flotation, however, do not limit this method of separation to a system containing water (14). Other liquids may be used, provided that the solid phase to be removed has only a partial or no affinity for the liquid.

The success of flotation has been in the development of reagents that are specific for one mineral or class of minerals and will thus form water-repellent surfaces thereon. Briefly, this is accomplished when a water-soluble, heteropolar, organic compound is added to a mixture of minerals and by chemical reaction or adsorption forms a surface coating on one mineral in preference to the others. As Wark (22) has shown, an air

bubble brought into contact with a clean mineral surface normally does not attach to it, as illustrated in Figure 1(a). If a suitable reagent is added, however, the selected mineral will acquire a water-repellent and air-avid surface as shown in Figure 1(b). Figure 2 shows galena particles clinging to air bubbles.

It is generally accepted that collector ions are adsorbed in the form of an oriented film, with the polar ends attached to the mineral and the nonpolar ends away from it (22). The surface reaction may be either reversible (17) or irreversible. Since the adsorbing ion is replacing hydrogen, hydroxyl, or other more strongly attached ions from the surface, and also since ionization of the collector seems to be necessary, pH is an important factor to be controlled (7).

The heteropolar compounds are classified either as anionic or cationic depending upon whether the adsorbing ion is negatively or positively charged. Anionic collectors are used in the great majority of present-day flotation operations. They may be grouped into classes based on the active, or polar groups, the most common of which are sulfhydryl (mercapto) or carboxylic (19). The sulfhydryl class includes types such as xanthates (see *Xanthic acids*) and thiophosphates (see *Thio acids*) with the general structural formulas:



where R is an alkyl group and M an alkali metal or ammonium ion. These compounds form relatively insoluble salts with heavy metals, but not with the alkaline earth metals. The carboxylic collectors are principally fatty acids or their soaps. They form collector coatings with either alkaline earth or heavy-metal ions. As an example: galena, PbS, may be floated away from calcite, CaCO<sub>3</sub>, by the use of sodium ethyl xanthate.

Conversely, calcite may be floated away from galena by the use of sodium oleate, but only if sufficient sulfide ions are present to mask the lead ions at the surface of the galena. The sulfide may be added as sodium sulfide. If excess sulfide ions are not present, both will float.

Cationic collectors came into use much later than the anionic class. They include quaternary ammonium, pyridinium, quinolinium, and sulfonium salts. A common type is represented by dodecylamine (laurylamine) salts, which may be used to float quartz, SiO<sub>2</sub>, and other minerals.

If other ions are present in solution, in addition to the hydrogen and hydroxyl ions, they exert profound effects on the attachment of collector ions to mineral surfaces, and thus give rise to a large class of so-called "modifying reagents." The first important use of a modifying agent was the activation of sphalerite, ZnS, with cupric ion derived from copper sulfate, so as to bring about the attachment of xanthate ions to the sphalerite by means of an ionic bridge. Another example is that of the activation of quartz with barium ions which are adsorbed on the quartz surface, and thus provide a positively charged surface for the adsorption of the negative oleate ion (9). Thus,



Fig. 2. Photomicrograph of galena particles in ethyl xanthate solution clinging to a small air bubble, which in turn is suspended from a larger air bubble 1 mm. in diameter.

when oleate is used as the collecting ion, the barium assists in providing the water-repellent coating and is called an "activator." On the other hand, if the collecting ion were the positive dodecylamine ion, then the positive barium ion would tend to prevent the attachment of the collecting ion and thus would become a "depressant" (20). Since the reactions under consideration take place at the surface of minerals, and also since only a partial monomolecular layer is required to produce flotation in most cases (7,21), the quantity of dissolved ion necessary to affect the reactions is extremely small. A concentration of a few parts per million of an undesirable ion will in many cases upset the desired conditions. Considering that most minerals are appreciably soluble in water and almost all ore bodies contain a large suite of minerals with a great variety of the chemical elements present as minor constituents, the chemistry of such systems becomes involved.

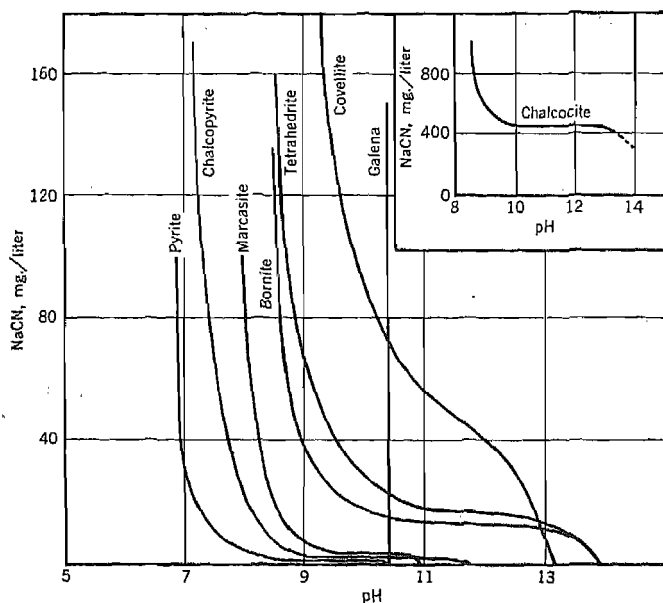


Fig. 3. Contact curves for several sulfide minerals (solution contains 25 mg./liter of potassium ethyl xanthate) (22).

An important class of modifying agents is the alkalis. Wark (22) states that their function in flotation may be (1) to precipitate harmful heavy-metal cations from solution, (2) to prevent activation of minerals whose flotation is not desired, or (3) to act as true depressants. Also the effectiveness of sodium cyanide and sodium sulfide is governed to such a large extent by the pH value, that these depressants are scarcely effective in the absence of alkalis. Wark has determined a set of curves by contact-angle measurements in which the conditions represented by the area to the left of each curve are for air-mineral attachment and hence flotation (see Fig. 3). The curves indicate that air would make contact with chalcopyrite,  $\text{CuFeS}_2$ , but not with pyrite at a pH value of 7.5, and a cyanide concentration of 30 mg. per liter. At these conditions, therefore, chalcopyrite would be floated, while pyrite would not.

**Physical factors** enter the flotation picture in a variety of ways. Once a particle has been prepared with a water-repellent surface, it must be brought into contact with

an air-water interface in such a manner that it will remain at that interface long enough for a separation to be effected. The most common method of producing these conditions is by the use of *froth flotation*, in which air bubbles are introduced into a pulp in any of a variety of ways. Agitation of the pulp, either by mechanical means or by the act of blowing large quantities of air through it, brings the particles into contact with air bubbles (16). If the force of attachment of the particle to the air bubble is sufficient to resist the shearing forces of gravitational and centrifugal pulls and the stripping force of pulp turbulence, the particle will rise to the surface of the pulp just as the basket of a free balloon will rise in air. The size and specific gravity of the mineral, the relative nonwettability of the mineral surface, and the turbulence and density of the pulp are all controlling factors. In general, mineral particles coarser than  $300\ \mu$  are not recovered by froth flotation.

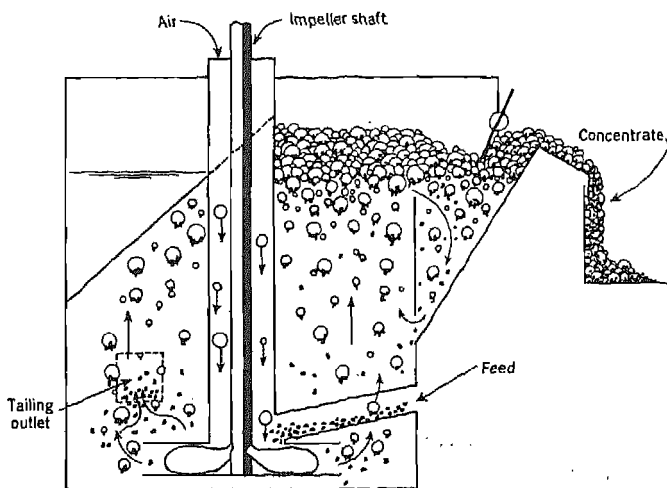


Fig. 4. Froth flotation cell.

In froth flotation, the mineral particles are collected at the surface of the pulp in a froth which is then scraped over a lip thus effecting a separation (see Fig. 4). To produce a froth that will be persistent enough to allow this separation, a number of frothing agents may be used, the most common of which is pine oil (an impure terpineol,  $C_{10}H_{17}OH$ ). Amyl alcohol and other higher alcohols are also used. Frothers function by changing the surface tension of the liquid. The froth serves a secondary purpose in providing a zone in which the unfloatable mineral particles and pulp that has been mechanically entrapped will drain away from the flotation concentrate.

Fine particles in the near-colloidal size range are difficult to recover by flotation. This is due in part to the mechanical difficulty of bringing fine particles into contact with air bubbles (18), and in part to the fact that the surfaces of fine particles are not the same as a freshly produced surface. Gaudin and Malozemoff (8) postulate that fine particles have a surface older on the average than coarse particles. Once a very fine particle is produced in a comminuting operation, the chances are very great that it will remain of that size until most of the solids are also reduced to that size. The fine particles, therefore, fail to acquire a constantly refreshed surface. A wide variety of chemical alterations may take place while a surface remains in contact with a complex aqueous solution, so that an old surface may fail to react with a collector when

added. Chemical alteration may be due to the chemical agents present in the grinding atmosphere (such as oxygen) and capable of dissolving in the pulp solution, and/or to those dissolved by the pulp solution from the solids present in the system (4).

Coarse particles, which may not be successfully recovered in standard flotation machines, are recovered in a number of ways, all of which may be included under the headings of *skin flotation* or *agglomeration*. Skin flotation may be effected by presenting a conditioned mineral surface to a quiescent water surface and allowing surface tension to hold it there, as in the classical experiment of floating a needle (6). If the liquid surface with the rafted mineral particles extends over a lip or a dam, the desired separation will result. A more common application of flotation principles to coarse particles may be found in the combination of agglomeration and gravity separation. The essence of this process is that particles with water-repellent surfaces tend to stick to air bubbles, oil droplets, or each other. Since the apparent specific gravity of a loose ball of many particles with an air bubble or oil droplet as a core is less than that of any one particle, and since the diameter of such a ball is much greater than that of the individual particles which have not been coated with a flotation collector, the well-known principles of gravity concentration for the separation of large, light particles from small, heavy particles may be employed. The machines used for this separation may be shaking tables, spiral concentrators, or other like devices.

### Operation

The successful operation of flotation requires a rather delicate balance of many operating variables, only some of which are under the direct control of the worker or engineer. The most important among these are the ore, the water, the reagents, the machines, and the method of combining the first three.

**Material Treated.** Most ore bodies consist of from one to five economically extractable metals or minerals combined with a much larger amount of a nonvaluable constituent referred to as "gangue." The texture or physical association of the minerals is one of the most important considerations, for it determines whether or not the valuable constituents may be removed and what degree of technology is required for the separation. It also dictates the selection of auxiliary operations such as comminution and gravity concentration. As a general rule, the most economical treatment is one in which a separation takes place at as coarse a size as possible to secure liberation of the minerals. If this size is coarser than that at which flotation is practiced, then other methods of concentration might be indicated. Likewise if the size of liberation is too fine to come within the flotation range, then chemical leaching might be the answer.

Probably without exception, no two ore bodies are identical and no single ore body is consistent in composition throughout. Ions of elements present in small quantities may seriously interfere with the desired separation. An added difficulty is that many deposits contain colloidal particles or "slimes" which tend to coat the surfaces of all minerals and thus hinder the selective action of flotation reagents (4).

**Water** supplies in adequate quantity and purity are necessary. If the supply is limited, then steps such as thickening may be used to recover the water from the final waste or "tailing." Soluble substances from the ore and flotation reagents accumulate in the recirculated water and may require special removal measures. If the supply water is contaminated either with inorganic salts or with organic material, then chemical

or other treatment may be required to purify it. Also to be considered is the water effluent from the plant. Stream-pollution laws are forcing more plants to re-use their water or to purify it before discharge into the public water supplies. Fortunately much of this purification can be accomplished by an additional flotation step (14).

**Flotation Reagents.** The choice of a reagent is made on the basis of its effectiveness, specificity, stability, ease of handling and addition, and cost per unit weight and per unit of recovery. The quantity added differs according to its function and may be varied to correct for variations in the ore and water input to the operation. Inorganic reagents are added to control pH and to provide activation or depression. Lime is the cheapest source of hydroxyl ion at a cost of a fraction of a cent per pound. Other common pH modifiers are sodium carbonate, sodium hydroxide, and sulfuric acid. Quantities added are usually in the range of a few pounds per ton of ore treated. Addition is made before or during flotation, as conditions require.

Organic reagents are added as collectors, frothers, and filming agents. Sulfhydryl collectors are usually added in amounts ranging from 0.05 to 0.25 lb. per ton of ore for the concentration of sulfides. Fatty acid collectors and cationic collectors of the amine type are added in quantities ranging from a fraction of a pound to a few pounds per ton of ore. Collectors are usually added as soluble salts at a point just ahead of the flotation machines. Since the collector must have time to dissolve, diffuse throughout the pulp, and react with the mineral surfaces, a special mixing tank or "conditioner" is often employed between the grinding circuit and the flotation cells. Reagents may also be added to the grinding circuit, in which case it becomes the conditioner, or, if the reaction is rapid, a reagent may be added directly to the flotation cells. Frothing agents, if required, are used in amounts of 0.05–0.15 lb. per ton. Excess frother will reduce the selectivity by producing too much froth, or, in extreme cases, will destroy the froth completely. Pine oil or other long-chain alcohols are the common frothing agents used. Filming agents are generally viscous, water-insoluble oils, used in conjunction with fatty acids for the flotation of porous minerals such as the pebble phosphates (see *Fertilizers*). Because of their insolubility, they must be used under conditions allowing maximum chance of contact with the mineral surface. This may be accomplished by stirring or tumbling a thick or viscous pulp of about 70% solids.

Table I shows a number of reagents used in flotation. The reagents listed represent a comprehensive but not complete summary of all reagents that have been tested for or applied to flotation problems. The statements of application are of necessity in general terms since certain reagents may be used for a multitude of problems and also any one problem usually requires several reagents. Quite often both cationic and anionic collectors are used in consecutive circuits under entirely different conditions to produce a satisfactory process. See also *Surface-active materials*.

**Pulp density** is important in both chemical and mechanical considerations. It determines reaction time and the quantity of reagent required to give desired reagent concentrations; hence, chemical factors argue for high pulp densities. On the other hand, mechanical factors place definite limits on the optimum density. Flotation is normally more rapid and complete in the denser pulps, but concentrate grade is lower; however, there appear to be some exceptions to this rule as noted by Ralston and King (13). The average range in practice seems to be about 35–40% solids by weight, although densities may run as high as 75% in unit cells according to Taggart (19). He also states that dense pulps are better suited to agitation machines and for the treatment of coarse mineral particles.



TABLE I. Flotation Reagents.

Reagent	Manufacturer	Composition	Form used	Amount used, lb./ton	Usual application
Aciterge					
Aerofloat 15	Commercial Am. Cy.	Fatty acid of a substituted oxazoline Thiophosphate reaction product of $P_2S_5$ with excess cresol	5-10% soln. Undiluted	0.25-1.00 0.05-0.20	Wetting agent, emulsifier Collector for metallic sulfides
Aerofloat 25	Am. Cy.	Similar to Aerofloat 15, but with less excess cresol	Undiluted	0.05-0.20	Collector for metallic sulfides
Aerofloat 31	Am. Cy.	Aerofloat 25 saturated with 6% thio-carbanilide	Undiluted	0.05-0.20	Collector for metallic sulfides
Aerofloat 203	Am. Cy.	Sodium diisopropyl dithiophosphate	5-10% soln.	0.05-0.20	Collector for metallic sulfides
Aerofloat 208	Am. Cy.	Sodium neutralized mixture of diethyl and di-sec-butyl phosphates	5-10% soln.	0.01-0.10	Collector for metallic sulfides
Aerofloat 213	Am. Cy.	$NH_4$ analog of Aerofloat 203	5-10% soln.	0.02-0.10	Collector for metallic sulfides
Aerofloat 226	Am. Cy.	Ammonium di-sec-butyl dithiophosphate	5-10% soln.	0.02-0.10	Collector for metallic sulfides
Aerofloat 238	Am. Cy.	Sodium di-sec-butyl dithiophosphate	5-10% soln.	0.02-0.10	Collector for metallic sulfides
Aerosol OT	Am. Cy.	Sodium bis(2-ethylhexyl) sulfosuccinate	1% soln.	0.01-0.20	Wetting agent
Aerosol AY	Am. Cy.	Sodium diamyl sulfosuccinate	1% soln.	0.01-0.20	Wetting agent
Aerosol MA	Am. Cy.	Sodium bis(1,3-dimethylbutyl) sulfosuccinate	1% soln.	0.01-0.20	Wetting agent
Aerosol OS	Am. Cy.	Sodium isopropylnaphthalenesulfonates	1% soln.	0.01-0.20	Wetting agent
Aerosol No. 18	Am. Cy.	Disodium <i>N</i> - <i>n</i> -octadecyl- $\beta$ -sulfosuccinamate	1% aq. soln.	0.01-0.20	Wetting agent
Aerosol No. 22	Am. Cy.	Tetrasodium <i>N</i> - <i>n</i> -octadecyl- <i>N</i> -(1,2-dicarboxyethyl)- $\beta$ -sulfosuccinamate	5-10% aq. soln.	0.01-0.20	Wetting agent
Albumin	—	Organic colloid of protein character	1-5% soln.	0.05-3.00	Depressant
Alcohols B-21 to B-30	Du Pont	Higher alcohols	Undiluted	0.05-0.50	Frothers
Aliphatic acids No. 50	Oronite	$C_6$ - $C_{12}$ aliphatic acids from petroleum naphtha	Undiluted or emulsified	0.25-3.00	Anionic collector
Aliphatic acids No. 100	Oronite	Sodium salt (soap) of aliphatic acids No. 50	1-5% soln.	0.25-3.00	Anionic collector
Aluminum sulfate	—	$Al_2(SO_4)_3 \cdot 18H_2O$	5-10% soln.	0.10-5.00	Slime flocculator, modifier
Amine 220	Armour, Carbide	A glyoxalidine (2-imidazoline)	1-10% soln.	0.10-0.50	Weak cationic collector

Amijel	Corn Products	Altered corn starch	1-10% soln.	0.10-2.00	Slime flocculator, depressant
Arnone-Phos	Am. Cy.	Monoammonium phosphate	Dry or soln.	0.50-3.00	Modifying agent
Armeen 8D <sup>a</sup>	Armour	Chiefly <i>n</i> -octylamine	Liquid or in isopropyl alcohol or kerosene solvent	0.05-1.00	Strong cationic collector
Armeen 10D	Armour	Chiefly <i>n</i> -decylamine	Liquid or in isopropyl alcohol or kerosene solvent	0.05-1.00	Strong cationic collector
Armeen 12D	Armour	Chiefly <i>n</i> -dodecylamine	In isopropyl alcohol or kerosene solvent	0.05-1.00	Strong cationic collector
Armeen 14D	Armour	Chiefly <i>n</i> -tetradecylamine	In isopropyl alcohol or kerosene solvent	0.05-1.00	Strong cationic collector
Armeen 16D	Armour	Chiefly <i>n</i> -hexadecylamine	In isopropyl alcohol or kerosene solvent	0.05-1.00	Strong cationic collector
Armeen 18D	Armour	Chiefly <i>n</i> -octadecylamine	In isopropyl alcohol or kerosene solvent	0.05-1.00	Strong cationic collector
Armeen CD	Armour	Mixture of normal octyl-, decyl-, dodecyl-, tetradecyl-, hexadecyl-, octadecyl-, octadecenyl-, and octadecadienylamines from coconut oil	Liquid or in isopropyl alcohol or kerosene solvent	0.05-1.00	Strong cationic collector
Armeen SD	Armour	Mixture of normal hexadecyl-, octadecyl-, octadecenyl-, and octadecadienylamines from soybean oil	Liquid or in isopropyl alcohol or kerosene solvent	0.05-1.00	Strong cationic collector
Armeen CSD	Armour	Mixture of normal hexadecyl-, octadecyl-, octadecenyl-, and octadecadienylamines from cottonseed oil	Liquid or in isopropyl alcohol or kerosene solvent	0.05-1.00	Strong cationic collector
Armeen TD	Armour	Mixture of normal hexadecyl-, octadecyl-, and octadecenylamines from tallow	In isopropyl alcohol or kerosene solvent	0.05-1.00	Strong cationic collector
Armeen HTD	Armour	Mixture of normal hexadecyl- and octadecylamines from hydrogenated tallow	In isopropyl alcohol or kerosene solvent	0.05-1.00	Strong cationic collector
Arnoflot SD	Armour	Mixture of normal hexadecyl-, octadecyl-, octadecenyl-, and octadecadienylamines and nitriles from soybean oil	Liquid or in isopropyl alcohol or kerosene solvent	0.05-1.00	Strong cationic collector

<sup>a</sup> See "Nitrogen derivatives" under *Fatty acids*.

*Continued*

TABLE I. Flotation Reagents (Continued).

Reagent	Manufacturer	Composition	Form used	Amount used, lb./ton	Usual application
Armec 8D <sup>a</sup>	Armour	Water-soluble acetate salt of Armeen 8D	1-5% aq. soln.	0.05-1.00	Strong cationic collector
Armec 10D	Armour	Water-soluble acetate salt of Armeen 10D	1-5% aq. soln.	0.05-1.00	Strong cationic collector
Armec 12D	Armour	Water-soluble acetate salt of Armeen 12D	1-5% aq. soln.	0.05-1.00	Strong cationic collector
Armec 14D	Armour	Water-soluble acetate salt of Armeen 14D	1-5% aq. soln.	0.05-1.00	Strong cationic collector
Armec 16D	Armour	Water-soluble acetate salt of Armeen 16D	1-5% aq. soln.	0.05-1.00	Strong cationic collector
Armec 18D	Armour	Water-soluble acetate salt of Armeen 18D	1-2½% aq. soln.	0.05-1.00	Strong cationic collector
Armec CD	Armour	Water-soluble acetate salt of Armeen CD	1-5% aq. soln.	0.05-1.00	Strong cationic collector
Armec SD	Armour	Water-soluble acetate salt of Armeen SD	1-5% aq. soln.	0.05-1.00	Strong cationic collector
Armec CSD	Armour	Water-soluble acetate salt of Armeen CSD	1-5% aq. soln.	0.05-1.00	Strong cationic collector
Armec TD	Armour	Water-soluble acetate salt of Armeen TD	1-5% aq. soln.	0.05-1.00	Strong cationic collector
Armec HTD	Armour	Water-soluble acetate salt of Armeen HTD	1-2½% aq. soln.	0.05-1.00	Strong cationic collector
Armecfloc SD	Armour	Water-soluble acetate salt of Armefloc SD	1-5% aq. soln.	0.05-1.00	Strong cationic collector
Arquad 8 <sup>a</sup>	Armour	Trimethyl- <i>n</i> -octylammonium chloride	1-5% aq. soln.	0.10-1.00	Weak cationic collector
Arquad 10	Armour	Trimethyl- <i>n</i> -decylammonium chloride	1-5% aq. soln.	0.10-1.00	Weak cationic collector
Arquad 12	Armour	Trimethyl- <i>n</i> -dodecylammonium chloride	1-5% aq. soln.	0.10-1.00	Weak cationic collector
Arquad 14	Armour	Trimethyl- <i>n</i> -tetradecylammonium chloride	1-5% aq. soln.	0.10-1.00	Weak cationic collector
Arquad 16	Armour	Trimethyl- <i>n</i> -hexadecylammonium chloride	1-5% aq. soln.	0.10-1.00	Weak cationic collector
Arquad 18	Armour	Trimethyl- <i>n</i> -octadecylammonium chloride	1-5% aq. soln.	0.10-1.00	Weak cationic collector

Arquad C	Armour	Trimethyl(Armeen CD)ammonium chloride	1-5% aq. soln.	0.10-1.00	Weak cationic collector
Arquad S	Armour	Trimethyl(Armeen SD)ammonium chloride	1-5% aq. soln.	0.10-1.00	Weak cationic collector
Arquad CS	Armour	Trimethyl(Armeen CSD)ammonium chloride	1-5% aq. soln.	0.10-1.00	Weak cationic collector
Arquad T	Armour	Trimethyl(Armeen TD)ammonium chloride	1-5% aq. soln.	0.10-1.00	Weak cationic collector
Arquad HT	Armour	Trimethyl(Armeen HTD)ammonium chloride	1-5% aq. soln.	0.10-1.00	Weak cationic collector
Barium chloride	—	BaCl <sub>2</sub>	1-5% soln.	0.01-1.00	Modifier for quartz
Bark extracts	—	Tannin and lignin compounds	1-5% aq. soln.	0.10-0.50	Depressant, slime dispersant
Barrett oils No. 4 and No. 634	Barrett	Coal-tar creosote oils	Undiluted	0.10-0.30	Frothers and froth modifiers
Black liquor	—	Source of tall-oil flotation reagents	—	—	—
Calgon <sup>b</sup>	Calgon	"Sodium hexametaphosphate"	1-5% aq. soln.	0.10-2.00	Slime dispersant
Caustic soda	—	Sodium hydroxide, flake or pellets, NaOH	5-10% aq. soln.	0.10-5.00	Modifier, slime dispersant
Copper sulfate	—	CuSO <sub>4</sub>	Dry or satd. soln.	0.20-5.00	Activator for sphalerite
Creosotes	—	Industrial grade wood- and coal-tar creosotes	Undiluted	0.05-0.50	Oil collectors and frothers
Cresols	—	Cresylic acids, CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH	Undiluted	0.05-0.20	Frother
Cupferron	—	Ammonium phenylhydrosulphohydroxyl-amine	—	—	Cationic collector for SnO <sub>2</sub>
Cyanide	—	NaCN or KCN	5% soln.	0.01-0.50	Depressant for sulfide minerals
Daxad No. 23	Dewey and Almy	Organic salts of alkylated aryl sulfonic acids	1-10% aq. soln.	0.05-1.00	Slime dispersant
DLT reagents	Ninol	Alkylated and acylated Nimols (C <sub>12</sub> H <sub>25</sub> ) <sub>2</sub> NH	Soln., emulsion	0.10-1.00	Collectors
Diamylamine	—	—	1-5% emulsion	0.05-0.20	Emulsifier, weak cationic collector
Dresinates	Hercules	Sodium, potassium, or ammonium salts (soaps) of selected rosin acids	1-5% soln.	0.20-3.00	Anionic collector
Dupanol 80	Du Pont	Sodium n-octyl sulfate	1-10% soln.	0.10-1.50	Anionic collector
Dupanol W. A. flakes	Du Pont	Sodium n-dodecyl sulfate	1-5% soln.	0.10-1.50	Anionic collector

<sup>a</sup> See "Nitrogen derivatives" under *Fatty acids*.

<sup>b</sup> See *Phosphoric acids*.

*Continued*

TABLE I. Flotation Reagents (Continued).

Reagent	Manufacturer	Composition	Form used	Amount used, lb./ton	Usual application
Emcol (Emulsol) 860B	Emulsol	1- <i>n</i> -Dodecylpyridinium iodide, $[C_{12}H_{25}NC_{12}H_{25}I]$	1-10% soln.	0.10-1.00	Cationic collector
Emcol X-1	Emulsol	Ammonium salt of <i>n</i> -dodecyl diethylene glycol sulfate	1-10% soln.	0.10-1.00	Anionic collector
Emcol X-25	Emulsol	Alkanolamine salt of a sulfated complex alcohol	1-5% soln.	0.10-0.50	Cationic collector
Emcol 607-40 (crude)	Emulsol	$[C_8H_5NCH_3CONHCH_2CH_2OOCR]Cl$	1-10% soln.	0.10-1.00	Anionic collector
Emulsol 660B, S-831, 903, 1336	Emulsol	Pyridinium salt wetting agents	1% soln.	0.005-0.50	Cationic collectors
Emulsol K-1249, 1339, 1340	Emulsol	Quaternary ammonium compounds with aliphatic substituents	1% soln.	0.005-0.50	Cationic collectors
Eucalyptus oil	—	—	Undiluted	0.05-0.20	Frother
Ferrous and ferric sulfates	—	$FeSO_4 \cdot H_2O$ and $Fe_2(SO_4)_3$	10% soln.	0.10-1.00	Sulfide depressant, quartz activator
Fish-oil fatty acids	Armour	Mixture of $C_{16}$ - $C_{24}$ saturated and unsaturated fatty acids	Liquid	0.25-1.00	Anionic collector
Flotagen and AC 400 series	Am. Cy.	2-Mercaptobenzothiazole derivatives	5% soln.	0.05-0.50	Collector (metallic sulfides and oxides)
Fluorspar	—	$CaF_2$ (pulverized)	Dry	1.00-5.00	Acid circuit for HF
Frother No. 52	Am. Cy.	Synthetic higher alcohols	Liquid	0.05-0.50	Frother
Frother No. 60	Am. Cy.	Synthetic higher alcohols	Liquid	0.05-0.50	Frother
Fuel oil	—	Crude and medium petroleum hydrocarbons	Liquid	0.50-5.00	Auxiliary collector
Gas oil	—	Petroleum hydrocarbons	Liquid	0.2-5.0	Auxiliary collector
Goulac	Miller	Calcium ligninsulfonate	5% soln.	0.5-2.0	Depressant for carbonaceous gangues
Glue	—	Organic colloid	5% soln.	0.1-0.5	Depressant and slime regulator
Hydrochloric acid	—	HCl	Liquid	0.20-5.00	Modifier, surface conditioner
Hydrofluoric acid	—	HF	Liquid	0.50-5.00	Silica depressant (cationic circuit)
Igepon T	Gen. Dyestuff	$C_{17}H_{33}CON(CH_3)C_2H_5SO_3Na$	1-5% soln.	—	Anionic collector

Indusoil	W.Va. Paper	Refined tall-oil acids	Liquid	0.5-2.0	Anionic collector
Invadine	Ciba	Sodium alkylbenzenesulfonate	5-10% soln.	0.2-0.5	Wetting agent
Kerosene	—	Water-white distillate from petroleum	Liquid, emulsion	0.10-2.50	Auxiliary or collector
Lactic acid	—	$\text{CH}_3\text{CHOHCOOH}$	Liquid	0.25-1.00	Depressant
Lead nitrate	—	$\text{Pb}(\text{NO}_3)_2$	5-10% soln.	0.50-1.50	Activator
Lime	—	Calcium hydroxide, $\text{Ca}(\text{OH})_2$	Slurry or dry	0.50-10.00	Modifier
Liqro	W.Va. Paper	Crude tall oil	Liquid emulsion	0.50-2.50	Anionic collector
Mahogany soap	Am. Cy.	Sodium salt of crude or refined petroleum sulfonic acids	5% aq. soln.	0.50-3.00	Anionic collector
Methylamyl acetate	Carbide	Water-white liquid, high boiling point	Liquid	0.05-0.10	Frother
Methylamyl alcohol <sup>a</sup>	—	Medium high-boiling alcohol	Liquid	0.05-0.10	Frother
(Methylamyl)amines	Sharples	Liquid short-chain amines	Liquid	0.05-0.20	Auxiliary cationic collector
Mixed amylamines	Phila. Quartz	Liquid short-chain amines	Liquid	0.05-0.20	Auxiliary cationic collector
Mercaptans	—	RSH (with R an alkyl or aryl group)	Diluted with alcohol	0.01-0.20	Collectors for sulfide minerals
Metso	Phila. Quartz	Sodium metasilicate pentahydrate	Dry or soln.	0.50-1.00	Slime dispersant
Minerec	Minerec	Dixanthogen (diethyl dithiobis[thionoformate])	—	0.01-0.10	Auxiliary sulfide collector
Nacconol	Natl. Aniline	Sodium alkylated aryl sulfonate	1-5% soln.	0.10-0.50	Wetting agent
Naphtheneic acid	—	Petroleum by-product, sp.gr. 0.95	Liquid	0.50-3.00	Weak anionic collector
No. 175	—	—	—	—	—
Neofat S-142	Armour	Mixture of oleic and linoleic fatty acids from distilled tall oil	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat D-142	Armour	Mixture of oleic and linoleic fatty acids from distilled tall oil	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat D-342	Armour	Pitch products from distilled tall oil	Liquid, emulsion	20-60	Binder for pellets
Neofat No. 3	Armour	Distilled linoleic and oleic fatty acids	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat No. 3R	Armour	Distilled linoleic and oleic fatty acids	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat No. 7	Armour	Caprylic acid	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat No. 9	Armour	Capric acid	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat No. 23	Armour	Distilled linoleic, oleic, and linolenic acids	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat No. 11	Armour	Lauric acid	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat No. 17	Armour	Saturated and unsaturated $\text{C}_{18}$ and $\text{C}_{20}$ fatty acids	Liquid, emulsion	0.20-2.00	Anionic collector

<sup>a</sup> See Vol. 1, p. 316.

Continued

TABLE I. Flotation Reagents (Continued).

Reagent	Manufacturer	Composition	Form used	Amount used, lb./ton	Usual application
Neofat No. 19	Armour	Unsaturated $C_{18}$ and $C_{20}$ fatty acids	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat DD cottonseed	Armour	Distilled palmitic, oleic, and linoleic acids	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat DD cornoil	Armour	Distilled palmitic, oleic, and linoleic acids	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat DD animal	Armour	Distilled palmitic, oleic, linoleic, and stearic acids	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat DD linseed	Armour	Distilled palmitic, oleic, linoleic, linolenic, and stearic acids	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat DD soybean	Armour	Distilled palmitic, oleic, linoleic, linolenic, and stearic acids	Liquid, emulsion	0.20-2.00	Anionic collector
Neofat DD palmoil	Armour	Distilled palmitic, oleic, and linoleic acids	Liquid, emulsion	0.20-2.00	Anionic collector
Ninol reagents	Ninol	Condensation products of an alkanol-amine and a fatty acid	Liquid, emulsion	0.10-1.00	Anionic and cationic collector
Nujol	Stanco	Refined white mineral oil	Liquid, emulsion	--	Collector, agricultural flotation
Orso	Procter	A blown neutral soap of vegetable origin	1-2% soln.	0.2-2.00	Anionic collector
Pelargonic acid	Emery	$CH_3(CH_2)_7COOH$ (synthetic)	Liquid, emulsion	0.1-2.00	Anionic collector
Pentasol No. 26	Sharples	An amyl alcohol of special distillation range	Liquid	0.05-0.20	Frother
Pine oil (Yarmour F)	Hercules	Terpineol, borneol, and fenchyl alcohol; terpenes (dipentene)	Liquid	0.05-0.50	Frother
Potassium permanganate	—	$KMnO_4$	5% soln.	0.10-2.0	Selective sulfide depressant
Potassium ethyl xanthate	Dow	$C_2H_5OCSSK$	10% soln.	0.05-0.15	Selective sulfide collector
Potassium <i>n</i> -butyl xanthate	Dow	$C_4H_9OCSSK$	10% soln.	0.05-0.15	Selective sulfide collector
Potassium <i>sec</i> -butyl xanthate	Dow	$C_4H_9OCSSK$	10% soln.	0.05-0.15	Selective sulfide collector
Potassium amyl xanthate	Dow	$C_5H_{11}OCSSK$	10% soln.	0.05-0.15	Selective sulfide collector
Potassium <i>n</i> -hexyl xanthate	Dow	$C_6H_{13}OCSSK$	10% soln.	0.05-0.15	Selective sulfide collector
Quebracho	—	Bark extract, a tannin product containing approx. 60% tannic acid	5-10% soln.	0.05-0.50	Depressant, slime dispersant

Reagent 610, etc. (600 series)	Am. Cy.	Colloidal organic modifiers	2-5% soln.	0.05-0.50	Slime dispersant, depressant
Reagent 708	Am. Cy.	Tall-oil fatty and rosin acids	Liquid, emulsion	0.50-3.00	Anionic collector
Reagent 712	Am. Cy.	A clear amber to dark brown paste	5-10% soln.	0.05-1.00	Anionic collector
Reagent 801 (800 series)	Am. Cy.	Soluble and dispersible high-molecular products	Liquid, emulsion, soln.	0.50-3.00	Anionic collector
Red oil	—	Oleic acid, commercial grade	Liquid, emulsion	0.20-2.00	Anionic collector
Risor	Hercules	A crude steam-distilled pine oil	Liquid	0.05-0.20	Frother
Sapamine MS	Ciba	$\text{Na}_2\text{CO}_3$ (white soluble powder)	Liquid	0.10-0.30	Cationic collector
Soda ash	—	Sodium diethyl dithiophosphate	Dry, 10-20% soln.	0.50-5.00	Slime dispersant, pH regulator
Sodium Aerofoat	Am. Cy.	$\text{NaHCO}_3$ (white soluble powder)	5-10% soln.	0.05-0.20	Selective sulfide collector
Sodium bicarbonate	—	$\text{CH}_3(\text{CH}_2)_9\text{SO}_3\text{Na}$	Dry, 10-20% soln.	0.50-5.00	pH buffer
Sodium n-hexadecyl sulfate	—	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	10% soln.	0.25	Collector for nonmetallic minerals
Sodium dichromate	—	$\text{NaF}$ (white powder)	Dry	0.2-5.0	Sulfide depressant
Sodium fluoride	—	$\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{CH}_2)_7\text{COONa}$	1-2% soln.	0.50-3.00	For HF in acid circuits
Sodium oleate	—	$\text{Na}_2\text{O}_3$	1-2% soln.	0.20-2.00	Anionic collector
Sodium peroxide	—	High-acid-value ( $\text{C}_3\text{-C}_{11}$ ) soaps	1-2% soln.	0.5-4.0	Sulfide depressant
Sodium soap of coconut oil	Armour	Soaps of vegetable and animal fatty acids	1-2% soln.	0.20-1.00	Anionic collector
Sodium soaps of fatty acids	Armour	"N" brand waterglass (variable $\text{Na}_2\text{O-SiO}_2$ ratio)	1-2% soln.	0.20-2.00	Anionic collector
Sodium silicate	Phila. Quartz	$\text{Na}_2\text{SiF}_6$ (white powder)	Liquid, soln.	0.20-5.00	Slime dispersant
Sodium fluosilicate	—	$\text{Na}_2\text{S}_9\text{H}_2\text{O}$	Dry	0.50-2.50	Depressant
Sodium sulfide	—	$\text{Na}_2\text{SO}_3$	5% soln.	0.5-5.0	Sulfide depressant
Sodium sulfate	—	$\text{Na}_2\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (water-soluble powder)	5% soln.	0.5-4.0	Sulfide depressant
Sodium pyrophosphate	—	$\text{C}_6\text{H}_5\text{OCSSNa}$	1-5% soln.	0.10-3.00	Dispersant, depressant
Sodium ethyl xanthate	Dow	$\text{C}_6\text{H}_5\text{OCSSNa}$	5-10% soln.	0.05-0.50	Selective sulfide collector
Sodium isopropyl xanthate	Dow	$\text{C}_6\text{H}_5\text{OCSSNa}$	5-10% soln.	0.05-0.50	Selective sulfide collector
Sodium sec-butyl xanthate	Dow	$\text{C}_6\text{H}_5\text{OCSSNa}$	5-10% soln.	0.05-0.50	Selective sulfide collector
Solox	U.S.	Denatured ethyl alcohol	5-10% soln.	0.05-0.50	Selective sulfide collector
Starch	Corn Prod., Staley	Vegetable protein, heat-treated, causticized, acid-treated	Liquid	0.05-0.25	Frother
			1-5% soln.	0.05-3.00	Slime flocculator, depressant

Continued



TABLE I. Flotation Reagents (Concluded).

Reagent	Manufacturer	Composition	Form used	Amount used, lb./ton	Usual application
Sulfuric acid	—	H <sub>2</sub> SO <sub>4</sub>	Liquid, soln.	0.20–10.00	Surface conditioner, pH regulator
Sulfur dioxide	—	SO <sub>2</sub>	3% satd. soln.	0.5–2.0	Selective sulfide depressant
Tall oil, crude	W.Va. Paper, Champion	Vegetable-origin (paper-industry) mixture of rosin, oleic, and linoleic acids	Liquid, emulsion	0.25–3.00	Anionic collector
Tall oil, distilled	Armour	Rosin acids reduced from 52 to 12 or 3%	Liquid, emulsion	0.25–3.00	Anionic collector
Tallso	W.Va. Paper	A crude tall-oil soap	1–10% soln.	0.50–5.00	Anionic collector
Tannic acid	—	Quebracho, and bark extract	1–5% soln.	0.05–1.00	Slime dispersant, depressant
Tergitol No. 4, 7	Carbide	Sodium <i>n</i> -dodecyl sulfate	5–10% soln.	0.20–1.00	Wetting agent, anionic collector
Terpineol	—	C <sub>10</sub> H <sub>17</sub> OH	Liquid	0.05–0.50	Frother
Thiocarbamide	—	1,3-Diphenyl-2-thiourea	Powder	0.05–0.15	Anionic collector
T-T mixture	—	15% thiocarbamide, 85% <i>o</i> -toluidine	Liquid	0.05–0.20	Anionic collector
Triphenylmethane dye	—	Brilliant Acid Green	—	—	Hematite collector
Trisodium phosphate	—	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	1–10% soln.	0.10–3.00	Slime dispersant, depressant
Triton K-60	Rohm & Haas	Dimethyl- <i>n</i> -hexadecylbenzylammonium chloride	Liquid	0.10–0.30	Cationic collector
Trostol	Champion	Crude tall oil	Liquid, emulsion	0.20–3.00	Anionic collector
Turkey red oil	Hercules	Sulfated and sulfonated castor oil	Liquid, emulsion	0.50–3.00	Anionic collector
Ultra Wet	Atlantic Refining Co.	Sodium alkylated aryl sulfonates	10–20% soln.	0.05–0.50	Wetting agent, weak collector
Waffle bark extract	—	Tannin product similar to quebracho	5–10% soln.	0.05–0.50	Slime dispersant, depressant
Yellow dextrin	—	Heat-treated starch	5–10% soln.	0.10–3.00	Slime dispersant, depressant
Zinc sulfate	—	ZnSO <sub>4</sub>	10% soln.	0.1–3.0	Zinc sulfide depressant

Am. Cy., American Cyanamid Co.; Armour, Armour and Co.; Barrett, The Barrett Division, Allied Chemical and Dye Corp.; Carbide, Carbide and Carbon Chemicals Co.; Calgon, Calgon, Inc.; Hagan Corporation; Champion, Champion Paper and Fiber Co.; Ciba, Ciba Company, Inc.; Commercial, Commercial Solvents Corp.; Corn Products, Corn Products Refining Co.; Dewey and Almy, Dewey and Almy Chemical Co.; Dow, Dow Chemical Co.; Du Pont, E. I. du Pont de Nemours & Co., Inc.; Emery, Emery Industries, Inc.; Emulsol, Emulsol Corp.; Gen. Dyestuff, General Dyestuff Corp.; Hercules, Hercules Powder Co.; Minerec, Minerec Corp.; Miller, Miller Chemical and Fertilizer Co.; Natl. Aniline, National Aniline Division, Allied Chemical and Dye Corp.; Ninol, Ninol, Inc.; Oronite, Oronite Chemical Co.; Phila. Quariz, Philadelphia Quariz Co.; Procter, The Procter & Gamble Co.; Rohm & Haas, Rohm & Haas Co., Inc.; Sharples, Sharples Chemicals, Inc.; Staley, Staley Manufacturing Co.; Stanco, Stanco, Inc.; U.S., U.S. Industrial Chemicals, Inc.; W.Va. Paper, West Virginia Pulp and Paper Co.

**Pulp Temperature.** Temperature of the pulp has an effect on the rate of reagent reaction. A high temperature aids completion of reactions involving decomposition, solution of solids, or formation of a gas as one of the reaction products, but ordinarily hinders reactions involving precipitation of solids (19). Flotation is usually carried on at normal pulp temperatures, frequently in the range of 12–20°C. Heated pulps are used in some copper–gold plants in northern Canada and in some plants for sphalerite flotation. Steam heating may also be used for the destruction and removal of collector coatings on copper concentrate in molybdenum–copper differential separations.

**Flotation Equipment.** Flotation machines are selected for a particular application on the basis of volume of pulp to be treated, speed of the flotation separation, the number of re-treatments of the concentrate required, the number of concentrates to be produced, the size of particles in the pulp, and other special considerations peculiar to the operation. Machines are designed with the aim of providing the maximum probability of contact between particle and bubble with the minimum of cost while producing the maximum possible separation. Efforts to attain these conflicting ideals have led to a large variety of machine types. Gaudin (6) classifies froth flotation cells in accordance with the mode of introduction of the gas as: (1) agitation cells in which air is drawn by a vortex caused by a rotating impeller; (2) subaeration cells in which air is introduced by suction or by blowing through or to the base of a rotating impeller; (3) cascade cells in which air is introduced by tumbling of the pulp; and (4) pneumatic cells in which air is introduced directly by blowing.

The common variables during operation are the height of the pulp in the cell and the degree of aeration. A lower pulp means a deeper froth layer and usually results in a cleaner froth overflow. A more intense aeration may provide a greater probability of particle–bubble contact, but may also result in a concentrate containing more undesirable impurities.

### Flotation Practice

It is impossible to state definitely the exact conditions for any one flotation separation because of the numerous variables involved and the constantly improving technology. Instead, it is probably useful to cite several examples of typical operations which illustrate conditions generally applicable to like materials.

**Lead–zinc ores** often consist of the minerals galena,  $\text{PbS}$ , sphalerite,  $\text{ZnS}$ , and a mixture of nonvaluable minerals such as quartz,  $\text{SiO}_2$ , pyrite,  $\text{FeS}_2$ , and calcite,  $\text{CaCO}_3$ . The galena–sphalerite separation is usually performed by grinding in the presence of sufficient lime or sodium carbonate to maintain a pH of 8–9.5 with an addition of 0.1–0.5 lb. of sodium cyanide per ton of ore treated. The combination of pH and cyanide is so selected as to prevent the flotation of the sphalerite while the galena is being recovered by the use of ethyl xanthate or dithiophosphate. A starvation quantity of frother (0.03–0.1 lb. pine oil per ton of ore) is used to provide only sufficient froth for the optimum recovery of a comparatively clean galena concentrate. The residue is further treated by the addition of sufficient copper sulfate to convert the free cyanide ion into a complex ion and to activate the sphalerite. Xanthate, frequently of a longer hydrocarbon chain than ethyl, is added as collector, and the frothing is made more vigorous. Each of the concentrates is usually re-treated by further flotation steps to aid in the elimination of entrapped minerals. The residues or “cleaner tailings” from these re-treatment steps are recirculated to the head of the respective “rougher” sections.

**Fine-coal flotation** is a much more recent development than sulfide or nonmetallic mineral flotation. Economic reasons hindered the application of flotation to the coal

TABLE II. Reagent Practice for Figure 5.

Point of addition	Reagent	Quantity added, lb./ton of ore
Ball mill	Soda ash	to pH 7.5
	Zinc sulfate	2.0
	Sodium cyanide	0.15
	Thiocarbamilide	0.10
Pb-Cu cells	Cresylic acid	0.04
Cu cells	Sodium dichromate	1.0
	Ethyl xanthate	0.05
	Cresylic acid	0.02
Zn conditioner	Lime	to pH 9.7
	Copper sulfate	0.08
Zn cells	Cresylic acid	0.06
	Ethyl xanthate	0.15

TABLE III. Assays and Recoveries for Figure 5.

Product	Weight, %	Lead		Copper		Zinc	
		Assay, %	Recovery, %	Assay, %	Recovery, %	Assay, %	Recovery, %
Original ore	100.0	15.26	100.0	3.62	100.0	12.78	100.0
Lead concentrate	20.3	69.50	92.8	0.70	4.0	4.90	7.9
Copper concentrate	9.0	5.45	3.2	36.40	90.4	13.25	9.2
Zinc concentrate	17.2	1.40	1.6	0.40	1.8	58.40	78.9
Tailings	53.5	0.71	2.4	0.25	3.8	1.01	4.0

industry. The technology of coal flotation is relatively simple. High-ash-content wastes from coal-cleaning plants are thickened, conditioned with fuel oil and pine oil, and floated in standard froth-flotation machines. In one anthracite plant (11) the ash content is reduced from 30% to less than 13% in a flotation step which makes a coal recovery of over 65%. Coal as coarse as 10 mesh is recovered. Reagent quantities are 1.92 lb. fuel oil and 0.54 lb. pine oil per ton of coal floated. The major problems are: (1) dewatering the concentrate so it can be readily handled in a form acceptable to the consumer and (2) marketing the product. The chief advantages are: (1) recovery of a substantial tonnage of coal which was formerly discarded and (2) elimination of stream pollution.

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**FLOUR.** See *Bakery processes and products; Cereals.*

**FLOW.** See *Fluid mechanics; Rheology.*

**FLOWMETERS.** See *Fluid mechanics (measurement).*

## FLUID MECHANICS

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See also *Film theory; Heat transfer; Hydraulic systems; Rheology.*

## PRINCIPLES

Fluid mechanics is the scientific treatment of the action of forces on fluids with particular emphasis on fluids in motion. Hence fluid mechanics is the interpretation of the physical behavior of fluids by application of the principles of conservation of mass and energy, and of Newton's laws of motion, with the useful result of deducing general rules that enable the engineer to predict the effects in engineering apparatus of changes in pressure, density, and velocity.

To the chemical engineer fluid mechanics is useful not only in predicting friction losses and interconversions of pressure and velocity, but also, and perhaps more importantly, in producing analogies among the transport of momentum, heat, and mass that provide a rational basis for the design of apparatus used in distillation, extraction, mixing and separating, and catalytic reactions. Thus the chemical engineer finds that the fundamental derivations are necessary for an informed attack on new problems and that these essentials are omitted in the summary, and often superficial, treatment to be found in the usual engineering handbook, which is largely concerned with predigested formulas and conventional applications.

It is the purpose of this article to present as rigorously as practicable the principles and techniques of fluid mechanics, proceeding through momentum, mass, and energy balances to the equations of motion, deriving theoretically many of the practical equa-

tions usually regarded as empirical, and emphasizing the assumptions and limitations involved in their use. Unfortunately, mathematics is indispensable in a quantitative treatment, and a large number of unfamiliar symbols are required to relate the many parameters, so that careful and thoughtful reading is requisite to understanding.

This treatment is intended to provide only the elements of the subject, presented as briefly as possible. Hunsaker and Rightmire (16) and Rouse (18) give a more extensive discussion at the elementary level, and Lamb (17) and Goldstein (15) provide more advanced treatment and many special applications.

### Definitions

A *fluid* is a substance that undergoes continuous deformation when subjected to a shear stress. A fluid may be considered as consisting of finite particles, each much larger than a molecule but infinitesimal compared to the total volume of fluid. The whole fluid is thus continuous, so that the action of forces on the particles is treated as producing relative motion, which results in translation, rotation, deformation, and shear, rather than impact.

*Consistency* is the property of a fluid in motion whereby forces arise in such a direction as to oppose the flow. Quantitatively, consistency is usually expressed as a coefficient which is the ratio of the shear stress to the velocity gradient (force per unit area divided by velocity change per unit distance perpendicular to the force).

A *Newtonian fluid* is one in which the consistency is independent of the shear stress, and hence of the rate of shear, and this constant coefficient when multiplied by  $g_c$  is numerically the *absolute viscosity* or *dynamic viscosity*, in English units (lb.-mass)/(ft.)(sec.). *Kinematic viscosity* is the ratio of absolute viscosity to density.

Some apparently fluid materials behave like elastic solids up to a yield point and then deform continuously with a resistance that is a function of the shear stress. Gels, soft metals, greases, and soaps are usually *complex* or *non-Newtonian* substances, and are often *thixotropic*, that is, deformation reduces the consistency. Other non-Newtonian substances such as slurries are *dilatant*, that is, deformation increases the consistency.

Both speed and direction are required to define a *velocity*, hence velocity is usually a vector quantity measured relative to a fixed-coordinate system. Rather than resort to vector analysis, however, it is preferable to use the more familiar spatial components of velocity; thus  $u$  is used to represent the velocity component in the  $x$  direction,  $v$  in the  $y$  direction, and  $w$  in the  $z$  direction. Since velocities fluctuate or vary in time, it is useful to represent a time-average of the velocity components as  $V_x$ ,  $V_y$ , and  $V_z$ . Similarly an overall mean velocity in the direction of flow is sometimes used. Thus the *mean mass velocity*,  $G$ , is the mass rate of flow through a cross section divided by the area of the cross section, and the *mean linear velocity*,  $V$ , is the mean mass velocity divided by the average density at the cross section. It is important to note that the mean linear velocity does not represent the speed of the fluid unless the flow is both steady and uniform.

*Steady flow* is motion where the velocity distribution is independent of time at any reference point, and usually implies that pressure, density, and temperature are also independent of time. *Uniform flow* is motion where the velocity is the same at every point at a given instant of time. *Incompressible flow* assumes that the density does not change throughout the path of flow. Liquids may be regarded as practically incom-

pressible except near the critical state and may usually be treated under incompressible flow. Although gases are highly compressible, they too may be treated under the assumptions of incompressible flow when the change in density produced by the motion is a small fraction of the normal density. Thus the effect of pressure on density during flow through an orifice may be neglected up to velocities equal to one-fifth the velocity of sound.

### Equations of Continuity

Many problems of engineering interest may be solved by means of mass, momentum, and energy balances. Such balances are called equations of continuity. Consider the control volume,  $B$ , shown in Figure 1, for which a general form of the conservation equation may be set up. The rate of accumulation of mass, momentum,

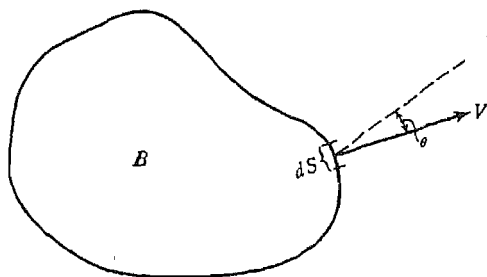


Figure 1.

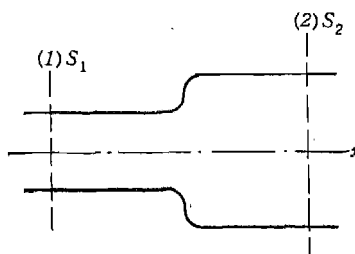


Figure 2.

and energy in the volume,  $B$ , is the sum of their rate of generation,  $R$ , inside the volume and their rate of transport through the surface,  $S$ . Letting  $n$  denote the concentration (amount per unit volume) of any of these entities:

$$\frac{\partial}{\partial t} \iiint_B n \, dB = \iiint_B R \, dB - \int_S n v \cos \theta \, dS - \int_S N \, dS \quad (1)$$

where the first term denotes the rate of accumulation, the second the rate of generation, the third the net rate of transport across the surface associated with the flow, and the fourth the net rate of transport across the surface by any other means.

### EQUATION OF CONTINUITY OF MASS

Let the quantity considered be the mass of the fluid. By definition, the concentration of mass is the density,  $\rho$ . Neglecting some possible applications concerning transformation of mass into energy or vice versa, the generation term vanishes. Similarly, since mass enters the volume by virtue of flow alone, the last term also vanishes. Then, interchanging the order of differentiation and integration:

$$\iiint_B \frac{\partial \rho}{\partial t} \, dB = - \int_S \rho v \cos \theta \, dS \quad (2)$$

For incompressible flow, or for compressible flow in steady state,  $\partial \rho / \partial t = 0$ , and:

$$\int_S \rho v \cos \theta \, dS = 0 \quad (3)$$

Equations (2) and (3) are forms of the equation of continuity. So, as an example, consider steady-state flow through the section of pipe shown in Figure 2. Here the control volume is bounded by the walls and sections (1) and (2). If the flow is perpendicular to the cross-sectional areas  $S_1$  and  $S_2$ ,  $\cos \theta = 1$ . Recognizing that fluid flows only through  $S_1$  and  $S_2$ :

$$\int_0^{r_2} \rho V_z 2\pi r \, dr - \int_0^{r_1} \rho V_z 2\pi r \, dr = 0 \quad (4)$$

where the first integral is taken over section (2) and the second over section (1). By definition of the volumetric average velocity,  $V$ :

$$V = \frac{1}{S} \int_0^{D/2} V_z 2\pi r \, dr \quad (5)$$

Thus one obtains for negligible radial variation of density:

$$S_2 V_2 \rho_2 = S_1 V_1 \rho_1 \quad (6)$$

and for constant cross section:

$$G_2 = G_1 \quad (7)$$

#### EQUATION OF CONTINUITY OF MOMENTUM

Consider now the transport of any component, say the  $x$  component of momentum. The momentum contained in any small volume  $dB$  is  $\rho V_x dB$ . Thus the momentum contained per unit volume, that is, the concentration,  $n$ , is  $\rho V_x = G_x$ . The rate of generation of  $x$ -momentum, by Newton's second law, must be a force. For instance,  $R$  in equation (1) may be the  $x$  component of the force of gravity per unit volume of fluid. The third term in this equation represents the net rate of transport of momentum associated with the flow. Finally, the last term in equation (1) represents the net rate of flow of momentum into the control volume associated with transfer of momentum on the molecular scale (or eddy scale if, in the third term, only transport in the mean flow is considered). The last term thus may be identified with the net shear force acting in the  $x$  direction on the surface,  $S$ , of the volume,  $B$ . Combining the forces represented by the second and fourth terms into a single net force acting in the  $x$  direction,  $F_x$ , and again interchanging the order of differentiation and integration:

$$g_c F_x = \int_B \int \int \frac{\partial G_x}{\partial t} \, dB + \int_S \int G_x v \cos \theta \, dS \quad (8)$$

where  $g_c$  is the proportionality factor appearing in Newton's second law,

$$F = \frac{1}{g_c} \frac{d(mv)}{dt}$$

Or, in steady state:



$$F_x = \frac{1}{g_c} \int_s \int G_x v \cos \theta \, dS \quad (9)$$

As a useful application of the momentum balance, consider a fluid flowing in a straight section of pipe as indicated in Figure 3. The net force,  $F_x$ , acting on the con-

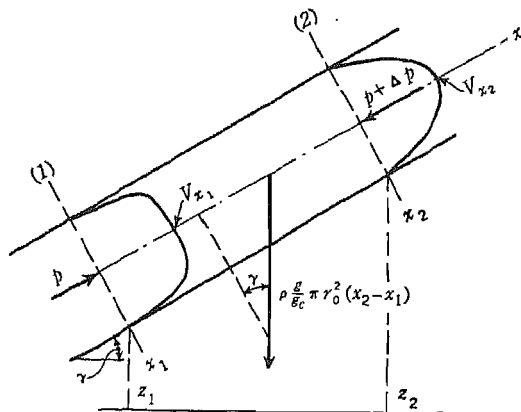


Figure 3.

trol volume isolated by the pipe and sections (1) and (2) is the sum of pressure, gravitational, and shear forces. The net pressure force acting in the  $x$  direction is:

$$p\pi r_0^2 - (p + \Delta p)\pi r_0^2 = -\Delta p\pi r_0^2$$

The shear force exerted on the fluid by the wall varies, in general, with the distance along the pipe. If at any distance  $x$  the shear stress at the wall is  $\tau_0$ , the net shear force acting on the control volume is:

$$\int_{x_1}^{x_2} 2\pi r_0 \tau_0 \, dx = -\bar{\tau}_0 2\pi r_0 (x_2 - x_1)$$

The gravitational force on the control volume with incompressible flow is:

$$\rho \frac{g}{g_c} \pi r_0^2 (x_2 - x_1)$$

the  $x$  component of which is:

$$-\rho \frac{g}{g_c} \pi r_0^2 (x_2 - x_1) \sin \gamma = -\rho \frac{g}{g_c} \pi r_0^2 (z_2 - z_1)$$

Remembering that the flow is everywhere perpendicular to the cross-sectional areas of sections (1) and (2),  $\cos \theta = 1$ . Thus equation (9) reduces to:

$$\begin{aligned} - \left[ \Delta p + \rho \frac{g}{g_c} (z_2 - z_1) \right] \pi r_0^2 - 2\pi r_0 \bar{\tau}_0 (x_2 - x_1) \\ = \frac{\rho}{g_c} \int_0^{D/2} 2\pi V_{x2}^2 r \, dr - \frac{\rho}{g_c} \int_0^{D/2} 2\pi V_{x1}^2 r \, dr \quad (10) \end{aligned}$$

Consider, now, the quantity:

$$\beta = \frac{\pi(D^2/4)V^2}{\int_0^{D/2} 2\pi V_{x'}^2 dr} \quad (11)$$

Then, from equations (10) and (11):

$$- \left[ \Delta p + \rho \frac{g}{g_c} (z_2 - z_1) \right] \pi r_0^2 - 2\pi r_0 \bar{\tau}_0 (x_2 - x_1) = \pi r_0^2 \rho \frac{V_2^2}{\beta_2 g_c} - \pi r_0^2 \rho \frac{V_1^2}{\beta_1 g_c} \quad (12)$$

When the velocity distributions at sections (1) and (2) are identical (as well as at any other section), that is, when  $\beta_1 = \beta_2 = \beta$ , the shear is uniformly distributed over the shear area. Thus, dropping the averaging index, for this case:

$$- \frac{\Delta p^*}{(x_2 - x_1)} \frac{r_0}{2} = \tau_0 \quad \text{where} \quad \Delta p^* = \Delta p + \rho \frac{g}{g_c} (z_2 - z_1) \quad (13)$$

If a similar analysis is performed on any axially symmetric fluid cylinder with a radius  $r$ :

$$- \frac{\Delta p^*}{L} \frac{r}{2} = \tau \quad \text{where} \quad x_2 - x_1 = L \quad (14)$$

Combining equations (13) and (14) one obtains the distribution of shear stress in the pipe:

$$\tau = \tau_0(r/r_0) \quad (15)$$

The shear stress is thus linear with the radius. This holds regardless of whether the flow is turbulent or laminar. However, note that equation (15) is only valid when the velocity distribution does not change as the fluid flows along the pipe. This is not always the case. For instance, at short distances after disturbances such as an entrance, a valve, or an orifice, the shear forces in equation (12) are negligible (since  $x_2 - x_1$  approaches zero) but the velocity distributions may change significantly. In such cases, as seen from equation (12), the pressure changes are due mainly to changes in  $\beta$ .

Equation (15) may be used to obtain the velocity distribution in a pipe provided the relationship between the shear stress and the velocity gradient is known. Consider a function  $\epsilon(\tau)$  such that:

$$dV_x/dr = -g_c \epsilon(\tau)/K \quad (16)$$

where  $K$  is some constant. For laminar flow of Newtonian fluids by definition of viscosity:

$$dV_x/dr = -g_c \tau/\mu \quad (17)$$

Hence:

$$\epsilon(\tau)/K = \tau/\mu \quad (18)$$

Therefore,  $\epsilon(\tau) = \tau$  and  $K = \mu$ . For non-Newtonian liquids  $\epsilon(\tau)/K$  may be obtained experimentally. When the flow is turbulent, equations developed by Prandtl and von Kármán may be used in conjunction with equation (16) to obtain  $\epsilon(\tau)/K$ . While the form of  $\epsilon(\tau)$  varies from case to case, the following development is limited only by the

assumptions leading to equation (15). Eliminating  $r$  from equations (15) and (16) and integrating:

$$V_r = \frac{g_c r_0}{K \tau_0} \int_{\tau}^{\tau_0} \epsilon(\tau) d\tau \quad (19)$$

Equation (19) describes the dependence of velocity on the shear stress,  $\tau$ , or, with the aid of equation (15), on the radius,  $r$ . Similarly, eliminating  $V_r$  and  $r$  from equations (5), (15), and (19):

$$\frac{V}{D} = \frac{g_c}{K \tau_0^3} \int_0^{\tau_0} \tau d\tau \int_{\tau}^{\tau_0} \epsilon(\tau) d\tau \quad (20)$$

which together with equation (14) yields a general relationship between flow rate and pressure drop. For example, eliminating  $\epsilon(\tau)/K$  and  $\tau$  from equations (14), (18), and (20) results in the well-known Poiseuille equation for pressure drop in tubes (laminar flow, Newtonian fluid):

$$\Delta p^*/L = 32\mu V/g_c D^2 \quad (21)$$

The application of these considerations to turbulent flow will be considered later. However, it is of interest at present to consider the variables affecting pressure drop in turbulent flow. For incompressible flow, gravity effects can be neglected. Then the shear stress  $\tau_0$  should depend only on  $V$ ,  $D$ ,  $\rho$ ,  $\mu$ , and the roughness,  $D/k$ . Hence, by dimensional analysis:

$$g_c \tau_0 / \rho V^2 = f(DV\rho/\mu, D/k) \quad (22)$$

Equation (22) forms the basis for the definition of the friction factor, in terms of which data on pipe-flow have been correlated. By definition:

$$f = 2g_c \tau_0 / \rho V^2 \quad (23)$$

It may be noted that some authors prefer to use the factor 8 instead of 2 in the above equation. Combining equations (13) and (23):

$$-\frac{\Delta p^*}{\rho} = 2f \frac{V^2}{g_c} \frac{L}{D} \quad (24)$$

the usual form of the pressure drop equation for turbulent flow in straight pipes.  $V^2/2g_c$  is the kinetic energy of one unit mass and is called "velocity head." Figure 8 shows the dependence of the friction factor on the Reynolds number,  $DV\rho/\mu$ , and the roughness. This chart is discussed in detail in a later section.

The momentum balance may also be used to obtain changes in pressure resulting from a sudden change in cross section of the pipe. Consider a control volume, shown in Figure 4, in the large section limited by sections (1) and (2). The latter is taken sufficiently far downstream to insure an approximately uniform velocity distribution but sufficiently close to section (1) to permit neglecting the frictional drag exerted by the wall of the large section. For these conditions, equation (9) reduces to:

$$(p_1 - p_2)S_2 = \frac{1}{g_c} \rho_2 S_2 V_2^2 - \frac{1}{g_c} \rho_1 S_1 V_1^2 \quad (25)$$

or with the aid of equation (6):

$$\frac{p_1 - p_2}{\rho_1} = \frac{V_1^2}{g_c} \left[ \frac{S_1^2 \rho_1}{S_2^2 \rho_2} - \frac{S_1}{S_2} \right] \quad (26)$$

A similar analysis can be applied to a sudden contraction. In Figure 5, if the friction loss between sections (1) and (2) is negligible, all the pressure loss is due to

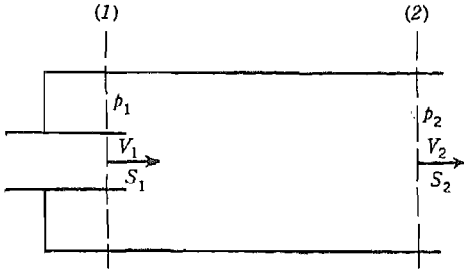


Figure 4.

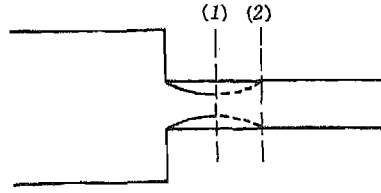


Figure 5.

expansion from the vena contracta. Then from equations (6) and (25), with the assumption of incompressible flow:

$$\frac{p_1 - p_2}{\rho} = \frac{V_2^2}{g_c} \left[ 1 - \frac{S_2}{S_1} \right] \quad (27)$$

and with a contraction coefficient defined by  $C_c = S_1/S_2$ :

$$\frac{p_1 - p_2}{\rho} = \frac{V_2^2}{g_c} \left[ 1 - \frac{1}{C_c} \right] \quad (28)$$

Measured values of  $C_c$  are given in Table I at corresponding values of the ratio of the areas in downstream and upstream pipes.

TABLE I.

Downstream area Upstream area	0.2	0.4	0.6	0.8	0.9	1.0
$C_c$	0.616	0.631	0.662	0.722	0.781	1.0
$\frac{1}{C_c}$	1.623	1.585	1.511	1.385	1.28	1.0
$\left(1 - \frac{1}{C_c}\right)^2$	0.39	0.34	0.26	0.15	0.05	0

#### THE EQUATION OF CONTINUITY OF ENERGY

Consider the transport of energy in a fluid. Neglecting applications concerning transformations between energy and mass, the second term in equation (1) vanishes. Experience shows that the energy associated with the flow may be considered as the sum of potential, kinetic, and internal energies. Thus:

$$E = \frac{g}{g_c} z + \frac{v^2}{2g_c} + U \quad (29)$$

where  $E$  is the energy residing in a unit mass. Then  $n = \rho E$ . The fourth term in equation (1) represents the net rate of transport of energy into the volume  $B$  exclusive

of the energy transport associated with the flow. This term, therefore, accounts for flow of energy in the form of heat (conduction and radiation) and work done on the control volume. The latter is the sum of shear (or shaft) work and flow work performed by the fluid outside  $B$  on the fluid inside  $B$ .

In a differential time,  $dt$ , a differential surface, moving with the fluid and approximately coinciding with a differential surface,  $dx$ , of  $B$  during the time interval,  $dt$ , describes a volume  $v \cos \theta dS dt$ . The rate at which flow work is being done through  $dS$  is  $p dS v \cos \theta$ . Thus, if  $q$  and  $w_s$  represent the flow of heat and rate of shear work per unit area:

$$N = -q - w_s + pv \cos \theta \quad (30)$$

Making the proper substitutions and exchanging the order of differentiation and integration in the first term of equation (1):

$$\begin{aligned} \int_B \int \int \frac{\partial}{\partial t} (\rho E) dB &= - \int_S \int \rho E v \cos \theta dS \\ &\quad - \int_S \int (-q - w_s + pv \cos \theta) dS \end{aligned} \quad (31)$$

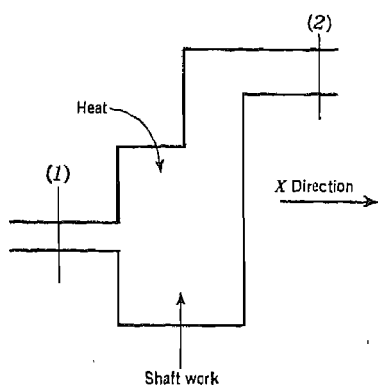


Figure 6.

Or, performing the first two integrations indicated in the last term of equation (31) and rearranging:

$$\begin{aligned} \int_B \int \int \frac{\partial}{\partial t} (\rho E) dB &= Q' + W'_s \\ &\quad - \int_S \int \left( \frac{p}{\rho} + E \right) \rho v \cos \theta dS \end{aligned} \quad (32)$$

In steady state:

$$Q' + W'_s = \int_S \int \left( \frac{p}{\rho} + E \right) \rho v \cos \theta dS \quad (33)$$

Equations (32) and (33) are general forms of the total energy balance.

If all parts of the surface  $S$  not consisting of fixed walls are normal to the flow, as is the case in the system shown in Figure 6,  $\cos \theta = 1$ , and  $v = V_x$ . Since the flow is perpendicular everywhere to  $S_1$  and  $S_2$ , no shear work is done. Hence  $W_s$  represents shaft work only. Expanding equation (33) with the aid of equation (29):

$$\begin{aligned} Q' + W'_s &= \frac{p_2}{\rho_2} \int_{S_2} \int \rho_2 V_x dS - \frac{p_1}{\rho_1} \int_{S_1} \int \rho_1 V_x dS + \frac{g}{g_c} z_2 \int_{S_2} \int \rho_2 V_x dS \\ &\quad - \frac{g}{g_c} z_1 \int_{S_1} \int \rho_1 V_x dS + \int_{S_2} \int \frac{V_x^3}{2g_c} \rho_2 dS - \int_{S_1} \int \frac{V_x^3}{2g_c} \rho_1 dS \\ &\quad + U_2 \int_{S_2} \int \rho_2 V_x dS - U_1 \int_{S_1} \int \rho_1 V_x dS \end{aligned} \quad (34)$$

Recognizing that by the equation of continuity:

$$\int_{S_1} \rho_1 V_x dS = \int_{S_2} \rho_2 V_x dS$$

is simply the mass rate of flow, one obtains after dividing equation (34) by this quantity,

$$Q + W_s = \frac{p_2}{\rho_2} - \frac{p_1}{\rho_1} + \frac{g}{g_c} (z_2 - z_1) + U_2 - U_1 + \frac{\int_{S_2} \int \frac{V_x^3}{2g_c} \rho_2 dS}{\int_{S_2} \int \rho_2 V_x dS} - \frac{\int_{S_1} \int \frac{V_x^3}{2g_c} \rho_1 dS}{\int_{S_1} \int \rho_1 V_x dS} \quad (35)$$

Consider a velocity distribution parameter  $\alpha$ , defined by:

$$\frac{V^2}{\alpha 2g_c} = \frac{\int_S \int \frac{V_x^3}{2g_c} \rho dS}{\int_S \int \rho V_x dS} = \frac{\int_S \int \frac{V_x^3}{2g_c} \rho dS}{V \rho S}$$

therefore:

$$\alpha = \frac{SV^3}{\int_S \int V_x^3 dS} \quad (36)$$

Then from equations (35) and (36):

$$Q + W_s + U_1 + \frac{p_1}{\rho_1} + z_1 \frac{g}{g_c} + \frac{V_1^2}{2\alpha_1 g_c} = U_2 + \frac{p_2}{\rho_2} + z_2 \frac{g}{g_c} + \frac{V_2^2}{2\alpha_2 g_c} \quad (37)$$

which is the usual form of the total-energy balance. Alternatively, since  $H = U + (p/\rho)$ :

$$Q + W_s + H_1 + z_1 \frac{g}{g_c} + \frac{V_1^2}{2\alpha_1 g_c} = H_2 + z_2 \frac{g}{g_c} + \frac{V_2^2}{2\alpha_2 g_c} \quad (38)$$

This form is convenient when the enthalpies at the two sections are known. Otherwise, the enthalpy difference may be evaluated from:

$$H_2 - H_1 = \int_{(1)}^{(2)} dH = \int_{(1)}^{(2)} \left( \frac{\partial H}{\partial T} \right)_p dT + \int_{(1)}^{(2)} \left( \frac{\partial H}{\partial p} \right)_T dp \quad (39)$$

or from thermodynamics:

$$H_2 - H_1 = \int_{(1)}^{(2)} c_p dT + \int_{(1)}^{(2)} \left[ \frac{1}{\rho} - T \left( \frac{\partial(1/\rho)}{\partial T} \right)_p \right] dp \quad (40)$$

For perfect gases, or for any fluid when the pressure changes are small, the third term of equation (40) vanishes. For liquids of constant density:

$$H_2 - H_1 = \int_{(1)}^{(2)} c_p dT + \frac{p_2 - p_1}{\rho} \quad (41)$$

In the general case, however, the usual  $p$ ,  $\rho$ ,  $T$  data are needed to evaluate the change in enthalpy.

#### THE MECHANICAL-ENERGY BALANCE

The mechanical-energy balance may be regarded as a definition of a dissipation term,  $\Delta F$ :

$$W_s + z_1 \frac{g}{g_c} + \frac{V_1^2}{2\alpha_1 g_c} + \frac{p_1}{\rho_1} + \int_{(1)}^{(2)} p d\left(\frac{1}{\rho}\right) = z_2 \frac{g}{g_c} + \frac{V_2^2}{2\alpha_2 g_c} + \frac{p_2}{\rho_2} + \Delta F \quad (42)$$

Alternatively, combining the pressure terms in equation (42):

$$W_s + z_1 \frac{g}{g_c} + \frac{V_1^2}{2\alpha_1 g_c} - \int_{(1)}^{(2)} \frac{dp}{\rho} = z_2 \frac{g}{g_c} + \frac{V_2^2}{2\alpha_2 g_c} + \Delta F \quad (43)$$

An interesting interpretation of the mechanical-energy balance may be obtained by subtracting equation (42) from equation (37):

$$U_2 - U_1 = Q - \left[ \int_{(1)}^{(2)} p d\left(\frac{1}{\rho}\right) - \Delta F \right] \quad (44)$$

Clearly, the integral in the above expression is the reversible work appearing in the rest of the fluid during the expansion of a unit mass that absorbs an amount of heat,  $Q$ , and the internal energy of which changes from  $U_1$  to  $U_2$  during the expansion. Due to the irreversibilities, the work done by a unit mass is less than the reversible work of expansion by an amount  $\Delta F$ . The latter, therefore, may be interpreted as the loss of available energy due to irreversible processes occurring between sections (1) and (2). In the case of isothermal, incompressible flow of a perfect gas:

$$U_2 = U_1 \quad \text{and} \quad \int_{(1)}^{(2)} p d\left(\frac{1}{\rho}\right) = 0$$

Then  $Q = -\Delta F$ , showing that an amount,  $\Delta F$ , of available energy is degraded to heat which must leave the system through the retaining walls.

In the sense discussed above, the mechanical-energy balance is simply a special form of the total-energy balance. It must be emphasized, however, that this interpretation in no way helps to evaluate the term  $\Delta F$ , since thermodynamics yields only qualitative information for irreversible processes. In general,  $\Delta F$  must be obtained from experiment, or by comparison of the mechanical-energy balance with the momentum balance. In either case the mechanical-energy balance supplies information in addition to that obtainable from the total-energy balance. When  $\Delta F$  vanishes, however, the total- and mechanical-energy balances may be used to yield the same information. For example, the flow of compressible fluids through Venturis and nozzles may be treated by using either balance. In each case the same expression is obtained for the flow in terms of the pressure drop. In cases of this nature, the choice of balance is dictated by convenience alone. In this connection it may be noted that the terms

in the total-energy balance may be evaluated from a knowledge of conditions existing at the sections under consideration. For the evaluation of the integral appearing in the mechanical-energy balance, however, a thermodynamic path, as well as an equation of state, must be available.

Turning now to the evaluation of  $\Delta F$ , consider first an incompressible fluid flowing in a straight section of pipe. If no shaft work enters this section, and if the velocity distribution between the sections chosen does not change, that is, if  $\alpha_1 = \alpha = \alpha_2$ , the mechanical-energy balance reduces to:

$$\frac{p_1}{\rho} + z_1 \frac{g}{g_c} - \left( \frac{p_2}{\rho} + z_2 \frac{g}{g_c} \right) = \Delta F_s \quad (45)$$

or,

$$-\Delta p^*/\rho = \Delta F_s \quad (46)$$

Comparing equations (46) and (24):

$$\Delta F_s = 2f \frac{V^2}{g_c} \frac{L}{D} \quad (47)$$

an expression known as the Fanning equation.

Consider now the friction loss due to a sudden expansion of an incompressible fluid. Referring to Figure 4, assume that the velocity over sections (1) and (2) is *uniform* ( $\alpha_1 = \alpha_2 = 1$ ). Then from the mechanical-energy balance:

$$\frac{p_1 - p_2}{\rho} + \frac{V_1^2 - V_2^2}{2g_c} = \Delta F_e \quad (48)$$

and from equation (26) (from momentum balance):

$$\frac{p_1 - p_2}{\rho} = \frac{V_1^2}{g_c} \left[ \left( \frac{S_1}{S_2} \right)^2 - \frac{S_1}{S_2} \right] \quad (49)$$

Comparing equations (48) and (49), and noting that from equation (6)  $S_1 V_1 = S_2 V_2$ :

$$\Delta F_e = \frac{V_1^2}{2g_c} \left[ 1 - \left( \frac{S_1}{S_2} \right)^2 \right] + \frac{V_1^2}{g_c} \left[ \left( \frac{S_1}{S_2} \right)^2 - \frac{S_1}{S_2} \right] \quad (50)$$

or,

$$\Delta F_e = \frac{V_1^2}{2g_c} \left[ 1 - \frac{S_1}{S_2} \right]^2 = \frac{(V_1 - V_2)^2}{2g_c} \quad (51)$$

The loss due to a sudden contraction may be obtained in a similar manner. From the mechanical-energy balance over sections (1) and (2) of Figure 5 together with equation (28):

$$\Delta F_c = \frac{V_2^2}{2g_c} \left[ 1 - \frac{1}{C_c} \right]^2 \quad (52)$$

Values for  $[1 - (1/C_c)]^2$  are shown for various values of the area ratio in Table I.

When the friction losses are due only to skin friction, sudden expansions, and sudden contractions:

$$\Delta F = \Delta F_s + \Delta F_e + \Delta F_c \quad (53)$$



For such cases, since  $\Delta F_s$ ,  $\Delta F_e$ , and  $\Delta F_c$  are evaluated with the aid of equations originating from the momentum balance, the mechanical-energy balance may be regarded as a restricted form of the former.

The skin-friction term in equation (47) includes an as yet undetermined friction factor,  $f$ . In order to express this factor in terms of the significant variables, a more detailed consideration of flow in pipes is necessary.

### Incompressible Flow in Pipes

One may distinguish between two types of flow: laminar and turbulent. In the former, regular flow patterns may be readily observed by injecting a filament of dye into the fluid. Such a filament maintains its identity for a comparatively long time, losing it eventually only as a result of molecular diffusion. This type of flow is observed at low velocities.

As the velocity of the fluid is increased above some critical value, turbulence sets in. The individual fluid particles (eddies) move in all directions in an erratic manner with velocities superimposed on the mean velocity. A filament of dye injected into a turbulent fluid field loses its identity almost instantaneously. It can be shown theoretically (see below) that the parameter determining the onset of turbulence is the Reynolds number:  $Re = DV\rho/\mu$ . From experiment it is known that the critical value of  $Re$  is approximately 2000. However, if elaborate precautions are taken to avoid entry disturbances, the critical value of  $Re$  may be pushed as high as 40,000.

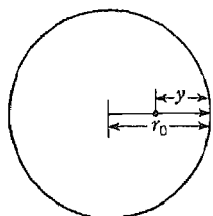


Figure 7.

Consider the distribution of the intensity of the velocity fluctuations with respect to the pipe radius. At the wall the fluctuations perpendicular to the wall must vanish. Hence, it is reasonable to expect that as the center of the pipe is approached, the fluctuations gain in intensity. This picture suggests the following schematic division of the series of flow in a pipe: (1) A *laminar sublayer* next to the wall; shear is transmitted on the molecular scale alone. (2) A *transition zone*; shear is transmitted to approximately the same degree by the molecules and by the fluctuating fluid masses. (3) *Turbulent core*; shear is transmitted by the fluctuating fluid masses. Effects of viscosity are negligible.

The mean velocity,  $V_x$ , should depend on the fluid properties  $\rho$  and  $\mu$ , on the radius of the pipe,  $r_0$ , on the pressure drop per unit length of pipe, as measured for instance by the shear stress at the wall,  $\tau_0$ , on the position in the pipe,  $y$  (see Fig. 7), and on the roughness,  $D/k$ . Then, by dimensional analysis:

$$\frac{V_x}{\sqrt{g_c \tau_0 / \rho}} = \omega \left( \frac{r_0 \sqrt{g_c \tau_0 / \rho}}{\nu}, \frac{y}{r_0}, \frac{D}{k} \right) \quad (54)$$

where the roughness is dimensionless. Defining  $V_x^* = \sqrt{g_c \tau_0 / \rho}$  (friction velocity) and  $Re^* = V_x^* r_0 / \nu$ :

$$V_x / V_x^* = \omega(Re^*, \xi, D/k) \quad (55)$$

where  $\xi = y/r_0$  is the position ratio.

For positions sufficiently near the wall, but outside the laminar sublayer, the curvature of the wall should have no effect on  $V_x$ . Thus,  $r_0$  may be dropped in equation (54). This results in one less dimensionless group in the expression for  $V_x/V_x^*$ :

$$V_x/V_x^* = \chi(V_x^*y/\nu, D/k) = \chi(Re^*J, D/k) \quad (56)$$

This is "Prandtl's wall-velocity law."

The difference between the velocity at the center and at any position is known as the velocity defect,  $V_{x, max.} - V_x$ . In the turbulent case the effect of viscosity and roughness should be negligible. Then  $V_{x, max.} - V_x$  is some function of  $\rho, \tau_0, r_0$ , and  $y$ . By dimensional analysis,

$$\frac{V_{x, max.} - V_x}{V_x^*} = \psi(\xi) \quad (57)$$

Equation (57), known as the "velocity-defect law," agrees well with experiment. The mean velocity defect,  $V_{x, max.} - V$ , may be obtained from equation (57) by integration, provided this equation is assumed to hold over the entire cross section of the pipe. Since the turbulent core occupies a large fraction of the volume of the pipe, this assumption results in negligible error. Then:

$$(V_{x, max.} - V)/V_x^* = \text{constant} \quad (58)$$

At this point it is convenient to introduce the friction factor,  $f$ . Eliminating  $V/V_x^*$  from equations (23) and (58):

$$\sqrt{2/f} = V_{x, max.}/V_x^* = \text{constant} \quad (59)$$

Restricting the argument to smooth pipes, application of equation (55) to the center line of the pipe yields:

$$V_{x, max.}/V_x^* = \omega(Re^*, l) = \Omega(Re^*) \quad (60)$$

Provided that  $\Omega(Re^*)$  is known, the friction factor may be obtained by eliminating  $V_{x, max.}/V_x^*$  from equations (59) and (60).

In the outer part of the turbulent core both the wall-velocity law and the velocity-defect law should hold. Eliminating  $V_x/V_x^*$  from equations (56) and (57):

$$\chi(Re^*\xi) = (V_{x, max.}/V_x^*) - \psi(\xi) = \Omega(Re^*) - \psi(\xi) \quad (61)$$

Differentiating this equation with respect to  $Re^*$ :

$$d\chi/dRe^* = \xi d\chi/d(Re^*\xi) = \chi'\xi = d\Omega/dRe^* \quad (62)$$

and with respect to  $\xi$ :

$$\chi'Re^* = -d\psi/d\xi \quad (63)$$

Since  $d\Omega/dRe^*$  is independent of  $\xi$ , one obtains from equation (62):

$$\chi' = f(Re^*)/\xi \quad (64)$$

and since  $d\psi/d\xi$  is independent of  $Re^*$ , from equation (63):

$$\chi' = f(\xi)/Re^* \quad (65)$$

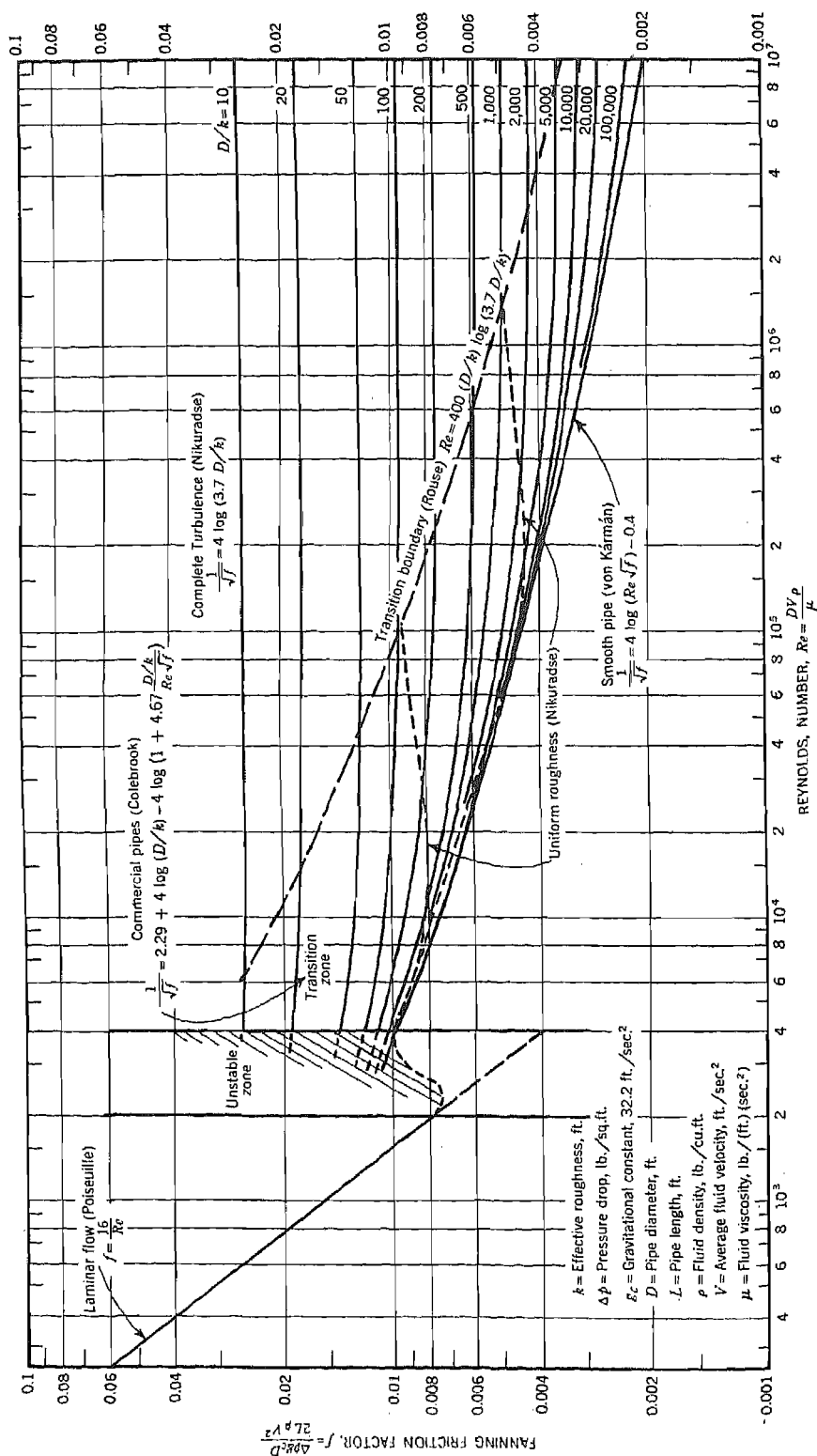


Fig. 8. Fanning friction factor for fluid flow in circular pipes.

The requirements stated in equations (64) and (65) can be met only if  $f(Re^*) = \text{constant}/Re^*$  and  $f(\xi) = \text{constant}/\xi$ . Then:

$$\chi' = A/Re^*\xi \quad (66)$$

where  $A$  is an undetermined constant.

Integrating equation (66):

$$\chi(Re^*\xi) = A \ln(Re^*\xi) + \text{constant} \quad (67)$$

Or combining equation (66) first with equation (62) and then with equation (63):

$$\Omega(Re^*) = A \ln Re^* + \text{constant} \quad (68)$$

$$\psi(\xi) = -A \ln \xi + \text{constant} \quad (68a)$$

Eliminating  $V_{x, \text{max.}}/V_x^*$  and  $\Omega(Re^*)$  from equations (59), (60), and (68):

$$\sqrt{2/f} = A \ln Re^* + \text{constant} \quad (69)$$

But:

$$Re^* = \frac{V_x^* r_0}{\nu} = \frac{2r_0 V}{\nu} \frac{V_x^*}{2V} = \frac{DV}{\nu} \frac{\sqrt{f/2}}{2} = \frac{Re\sqrt{f/2}}{2} \quad (70)$$

Finally from equations (69) and (70):

$$1/\sqrt{f} = A_1 \log(Re \sqrt{f}) + A_2 \quad (71)$$

Or by comparison with experiment:

$$1/\sqrt{f} = 4 \log(Re \sqrt{f}) - 0.4 \quad (72)$$

Equation (71) is known as the von Kármán equation for friction in smooth pipes. A plot of this equation is shown in Figure 8.

This figure also shows as dotted lines Nikuradse's experiments on the effect of roughness on pipe friction. The pipes were artificially roughened by a coating of sand grains of uniform size. The roughness is represented by the parameter  $D/k$ , where  $k$  is the diameter of the grains. If one assumes that the roughness is so great that viscosity does not influence the flow, an analysis similar to the one leading to equation (71) results in:

$$\frac{1}{\sqrt{f}} = 4 \log \left( 3.7 \frac{D}{k} \right) \quad (73)$$

where the numerical values are obtained from the experiments of Nikuradse. For commercial pipes Colebrook proposed:

$$\frac{1}{\sqrt{f}} = 2.29 + 4 \log \left( \frac{D}{k} \right) - 4 \log \left( 1 + 4.67 \frac{D/k}{Re\sqrt{f}} \right) \quad (74)$$

an equation which reduces in the limiting cases of very small and very great roughness to equations (72) and (73), respectively.

Since the random roughness found in commercial pipes produces greater turbulence than the regular roughness of Nikuradse's experiments, the higher friction factors obtained from equation (74) should be used.

The turbulent velocity distribution in smooth pipes is obtained by combining equations (56) and (67):

$$\frac{V_x}{V_x^*} = 5.75 \log \left( \frac{V_x^* y}{\nu} \right) + 5.5 \quad (75)$$

the numerical values being obtained by comparison with Nikuradse's data. Figure 9 shows a plot of equation (75), together with Nikuradse's data. Here the velocity

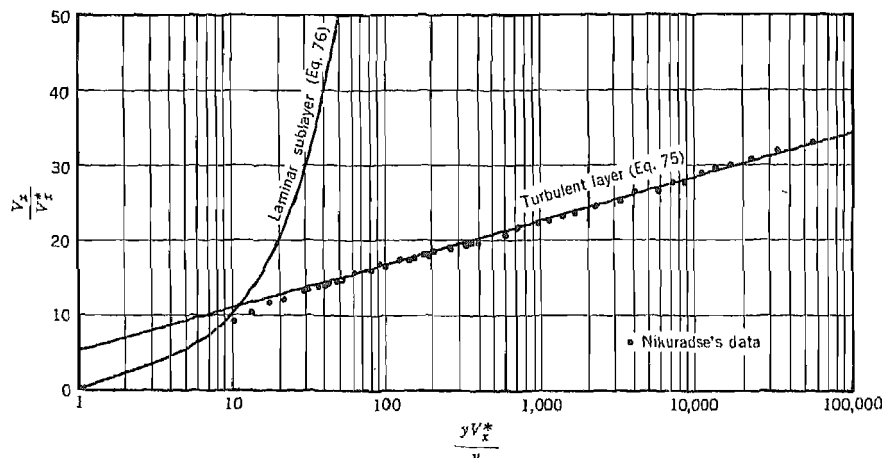


Fig. 9. Velocity distribution in a smooth pipe.

distribution in the laminar sublayer is obtained as follows: Since every point in the laminar sublayer is very near the wall, it follows from equation (15) that:

$$\tau \cong \tau_0 \cong \frac{\mu}{g_c} \frac{dV_x}{dy}$$

Since  $\tau$  is approximately constant at  $\tau_0$ ,  $dV_x/dy$  must also be approximately constant. Then:

$$\frac{dV_x}{dy} = \frac{V_x}{y} \quad \text{and} \quad \tau_0 = \frac{\mu V_x}{g_c y}$$

Therefore:

$$\frac{V_x}{V_x^*} = \frac{V_x^* y}{\nu} \quad (76)$$

Equation (75) is a good fit of the experimental data for  $V_x^* y/\nu > 30$ . Below this value the data deviate from the line representing equation (75), tending to approach the curve representing equation (76) at  $V_x^* y/\nu = 5$ . Hence, one obtains for the thickness,  $\delta$ , of the laminar sublayer,  $\delta V_x^*/\nu = 5$ .

The arguments presented up to this point were based on dimensional analysis and some judicious assumptions. From consideration of the mechanism of turbulent momentum transfer, Prandtl and von Kármán have obtained more fundamental and far-reaching solutions. Let  $dS$  denote a differential part of the surface enclosing any axially symmetric cylinder of fluid. The concentration of the axial component of

momentum at  $dS$  is  $\rho uv$ . The instantaneous efflux of momentum from the fluid cylinder through  $dS$  is therefore  $\rho uv dS$ , where  $u$  and  $v$  are the axial and radial components of the instantaneous velocity. For instance,  $u = V_x + u'$ ;  $v = V_y + v' = v'$ . Here  $u'$  and  $v'$  are the instantaneous fluctuating velocities superimposed on the mean velocities by turbulence. Hence:

$$V_x = (1/t) \int_0^t u dt = (1/t) \int_0^t (V_x + u') dt \quad (77)$$

where  $t$  is a time interval, sufficiently large to include a large number of fluctuations. From equation (77):

$$\overline{u'} = (1/t) \int_0^t u' dt = 0 \quad (78)$$

similarly:

$$\overline{v'} = (1/t) \int_0^t v' dt = 0 \quad (79)$$

By Newton's second law, the momentum flowing through  $dS$ ,  $\rho uv dS$ , is the force exerted by the cylinder on the remainder of the fluid. Then, by Newton's third law, the force exerted by the remainder of the fluid on the cylinder is equal in magnitude, but opposite in sign. Dividing this force by  $dS$  and taking a time average, one obtains:

$$g_c \tau_t = -\overline{\rho uv} = -\overline{\rho(V_x + u')v'} = -\overline{\rho V_x v'} - \overline{\rho u'v'} \quad (80)$$

an expression for the turbulent shear stress. For incompressible flow the density may be removed from under the averaging sign. Then, taking equation (79) into account:

$$\tau_t = -(\rho/g_c) \overline{u'v'} \quad (81)$$

Since either  $u'$  or  $v'$  may be positive or negative, there are two ways for  $u'v'$  to be negative and two ways for it to be positive. Therefore, if no correlation exists between  $u'$  and  $v'$  (isotropic turbulence),  $\overline{u'v'} = 0$ . By virtue of the velocity gradients existing in pipes, however, a correlation does in general exist. Defining a correlation coefficient by:

$$R_1 = \overline{u'v'}/\sqrt{\overline{u'^2}}\sqrt{\overline{v'^2}} \quad (82)$$

and eliminating  $\overline{u'v'}$  between equations (81) and (82):

$$\tau_t = -(\rho R_1/g_c) \sqrt{\overline{u'^2}} \sqrt{\overline{v'^2}} \quad (83)$$

The turbulent shear is thus expressed in terms of the mean square velocity fluctuations.

Expressions for the intensity of the fluctuations may be obtained from a consideration of von Kármán's similarity hypothesis. According to this hypothesis the turbulent patterns at various points in the flow field are geometrically and kinematically similar. Geometric similarity of patterns (for example, similar triangles) is a familiar concept. It simply means that the ratio of corresponding dimensions for two patterns is a constant. This principle may be restated as follows: geometric similarity between two patterns exists if all corresponding dimensions are equal, provided that these are measured by a suitably chosen length scale for each pattern. Kine-

matic similarity between flow patterns is said to exist if geometric similarity exists and if the times for corresponding events in two flow patterns are equal, provided these times are measured by a suitably chosen time scale for each pattern. Kinematic similarity implies that all functions of the flow pattern having physical dimensions which can be synthesized from length and time should be invariant with respect to any translation, provided the function is always measured in terms of the suitably chosen length and time scales.

Let the units of length at two points in the turbulent flow field be  $l_1$  and  $l_2$ , respectively. As units of time, it is convenient to choose the reciprocals of the velocity gradients at the two points:  $(dy/dV_x)_1$  and  $(dy/dV_x)_2$ . Clearly, then, the unit of velocity at any point in the turbulent flow field is  $l(dy/dV_x)$ . Since the numerical value of  $l$  is so far unspecified, it is permissible to specify arbitrarily the value of the unit of velocity. In particular, the velocities may be measured in terms of the intensity of the fluctuations. Hence:

$$l(dy/dV_x) = \sqrt{\overline{u'^2}} \quad (84)$$

Here  $l$  is called the convection path or the mixing length. In general, a bar indicates the average of the quantity under the bar.

Prandtl was the first to obtain equation (84). His considerations, however, were based on an idealization of the continuous mixing process. He assumed that an eddy retained its original momentum until it had moved a distance  $l$ . Thereafter, the eddy was supposed to blend suddenly and completely with the surrounding fluids. When viewed in this light, the mixing length corresponds to the mean free path of molecular motion. The analogy is, however, far fetched, and it is better to regard the mixing length as being derived from the similarity hypothesis.

Assuming that  $\sqrt{\overline{y'^2}}$  is proportional to  $\sqrt{\overline{u'^2}}$ , and combining this constant with the correlation coefficient  $R_1$ , one obtains from equations (83) and (84):

$$\tau_t = (\rho l^2/g_c)(dV_x/dy)^2 \quad (85)$$

an equation first obtained by Prandtl. The variation of mixing length with pipe radius has been obtained by Nikuradse from experimental data on velocity distribution. His results show that the mixing length is relatively insensitive to the Reynolds number. For most of the range of the position ratio the following empirical equation is a good fit of the data:

$$l = cy \sqrt{1 - (y/r_0)} \quad (86)$$

where  $c$  is a constant. An expression for the velocity distribution may now be obtained by assuming that the molecular shear is negligible compared to the turbulent shear:  $\tau = \tau_t$ . Eliminating  $\tau_t$  and  $l$  from equations (15), (85), and (86):

$$\frac{dV_x}{dy} = \frac{1}{cy} \sqrt{\frac{g_c \tau_0}{\rho}} \quad (87)$$

or:

$$dV_x/dy = V_x^*/cy \quad (88)$$

Upon integration:

$$V_x/V_x^* = (1/c) \ln y + \text{constant} \quad (89)$$

or, realizing that  $V_x^*/\nu$  is constant:

$$V_x/V_x^* = (1/c) \ln (V_x^*y/\nu) + \text{constant} \quad (90)$$

This is "Prandtl's logarithmic velocity distribution law" and is seen to be identical with equation (75).

An analytical expression for the mixing length can be obtained by further considering the von Kármán similarity hypothesis. Consider the function:

$$\frac{dV_x}{dy} \bigg/ \frac{d^2V_x}{dy^2}$$

This function has the dimension of length. For kinematic similarity, it must be invariant with respect to any translation in the turbulent field, provided it is measured at all times in terms of the previously chosen unit of length,  $l$ . If:

$$y_s = y/l \quad (91)$$

$y_s$  is measured in terms of the proper unit. Then:

$$\frac{d^2V_x}{dy_s^2} \bigg/ \frac{dV_x}{dy_s} = l \frac{d^2V_x}{dy^2} \bigg/ \frac{dV_x}{dy} \quad (92)$$

As already stated, the left side of equation (92) must be invariant with respect to translation. Hence the right side must also be invariant and:

$$l = -\kappa \frac{dV_x}{dy} \bigg/ \frac{d^2V_x}{dy^2} \quad (93)$$

where  $\kappa$  is a universal constant known as the von Kármán constant.

Another differential equation for the velocity distribution may now be obtained by eliminating  $\tau$  and  $l$  from equations (15), (85), and (93) and remembering that  $V_x^* = \sqrt{g_c \tau_0 / \rho}$ :

$$\frac{d(dV_x/dy)}{(dV_x/dy)^2} = -\frac{\kappa}{V_x^*} \frac{dy}{\sqrt{1 - (y/r_0)}} \quad (94)$$

Von Kármán integrated this equation by assuming an infinite velocity gradient at the wall, and obtained:

$$\frac{V_{x, \max} - V}{V_x^*} = -\frac{1}{\kappa} \left[ \log \left( 1 - \sqrt{1 - \frac{y}{r_0}} \right) + \sqrt{1 - \frac{y}{r_0}} \right] \quad (95)$$

This equation is a good fit of experimental data and represents a considerable triumph for the similarity hypothesis, although the logarithmic velocity distribution in equation (90) is better. It must be remembered, however, that in arriving at equation (90) the experimental data have already been used in the form of equation (86).

### Differential Equations of Fluid Mechanics

In the preceding sections balances of mass, momentum, and energy over finite volumes have been used. These balances may also be used to obtain useful differential equations. The derivation of these equations may be found elsewhere and need not be repeated here (17,18). It is pertinent, however, to consider how the application



of simplifying assumptions to these equations led to the development of such familiar concepts as Bernoulli's theorem, the Reynolds number, and Stokes' law.

The equation of continuity in differential form is:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial G_x}{\partial x} - \frac{\partial G_y}{\partial y} - \frac{\partial G_z}{\partial z} \quad (96)$$

In steady state, for incompressible fluids:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \quad (97)$$

Note that these equations provide a relationship between the various components of the velocity. For instance, in two-dimensional flow, if  $u(x, y)$  is known,  $v$  may be obtained from:

$$v = - \int \frac{\partial u}{\partial x} dy \quad (98)$$

With the aid of the equation of continuity, the differential equation for the conservation of momentum may be put into the form known as the Navier-Stokes equations of motion. For incompressible fluids for the  $x$  direction,

$$g_c X - \frac{g_c}{\rho} \frac{\partial p}{\partial x} + \nu \left[ \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right] = \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z} \quad (99)$$

All terms in equation (99) may be regarded as forces acting on a unit mass of fluid. The first term represents the  $x$  component of the body forces (for example, force of gravity), the second is the force that arises from the existence of a pressure gradient, the third term represents shear forces, the fourth term the temporal part of the inertia forces (acceleration due to changes of velocity at a given point), and the last three terms the spatial part of the inertia forces (acceleration due to change of velocity with position).

Equation (99) is nonlinear, and solutions can be found only for special cases by neglecting some of the terms. Consider, for instance, an ideal fluid whose viscosity vanishes. While no such fluids exist, the assumption of ideality is permissible for fluids of low viscosity at sufficient distances from boundaries. Then  $\nu \cong 0$ , and:

$$g_c X - \frac{g_c}{\rho} \frac{\partial p}{\partial x} = \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z} \quad (100)$$

known as the *Euler equation*. Of course, there are two similar equations for  $v$  and  $w$ . Assuming that the body forces are derivable from a potential (for example, gravitational potential) and assuming that infinitesimal fluid particles have no rotational motion, it can be shown that:

$$\partial u / \partial y = \partial v / \partial x; \quad \partial u / \partial z = \partial w / \partial x \quad (101)$$

and furthermore that there exists a function,  $\phi$ , called the velocity potential, such that:

$$u = -\partial \phi / \partial x; \quad v = -\partial \phi / \partial y; \quad w = -\partial \phi / \partial z \quad (102)$$

Under these conditions for steady-state incompressible flow it can be shown that:

$$\frac{u_1^2}{2} + g_c \frac{p_1}{\rho_1} + gz_1 = \frac{u_2^2}{2} + g_c \frac{p_2}{\rho_2} + gz_2 \quad (103)$$

where subscripts 1 and 2 refer to two points in the field of flow. Equation (103) is known as *Bernoulli's theorem*, which should not be confused with the mechanical-energy balance. For irrotational flow from equations (97) and (102):

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0 \quad (104)$$

The general procedure in arriving at the solution of a flow problem, for which the assumptions used to obtain equation (103) are valid, is to solve equation (104) (the *Laplace equation*) for  $\phi$ , thus obtaining from equation (102)  $u$ ,  $v$ , and  $w$ . Bernoulli's theorem may then be used to solve for the pressures.

If we consider the ratio of the inertia forces and viscous forces appearing in equation (99), assuming steady state and retaining only the representative terms, this ratio becomes:

$$u \frac{\partial u}{\partial x} / \nu \frac{\partial^2 u}{\partial x^2}$$

Let  $u_0$  be some representative velocity, and  $x_0$  some representative dimension such that the velocity  $u$  is of the order  $u_0$  and the distances  $x$  are of the order  $x_0$ . Then the ratio of the inertia and viscous forces is the Reynolds number,  $u_0 x_0 / \nu$ . Whenever the Reynolds analogy is applied, it is essential to establish the proper criteria.

As an example, consider the criteria for application of Stokes' law. Stokes obtained his familiar drag law by solving equation (99) with the assumption that the inertia terms (and also the body forces) are negligible with respect to the viscous forces; hence:

$$g_c F_x = 6\pi\mu r_0 u_0 = 3\pi\mu DV \quad (105)$$

where mean relative velocity,  $V$ , is taken as the representative velocity,  $u_0$ , and the diameter,  $D$ , of the sphere is taken as the representative distance,  $x_0$ . Thus the drag is independent of the fluid density and varies with the first power of the relative velocity when the inertia terms are negligible, that is, when the Reynolds number,  $DV/\nu$ , is less than unity.

As a less well-known example consider the applicability of Stokes' law to spherical particles moving in a high-frequency sonic field. To obtain the necessary criterion (in addition to the one derived above) divide the temporal part of the inertia forces by a representative viscous term to obtain:

$$\frac{\partial u}{\partial t} / \nu \frac{\partial^2 u}{\partial x^2}$$

Taking  $u_0$  and  $x_0$  as before and using the representative time as  $1/f'$  (where  $f'$  is the frequency of the sound wave), one obtains for the required criterion  $f'x_0^2/\nu \ll 1$ .

On the other hand, when the viscous forces are negligible with respect to the inertia terms, at Reynolds numbers from 1,000 to 200,000, the drag is independent of the

fluid viscosity and is proportional to frontal area, fluid density, and the square of relative velocity. Thus:

$$g_c F_z = C_D \frac{\pi D^2}{4} \frac{\rho V^2}{2} \quad (106)$$

### Pressure Losses in Process Apparatus

#### CONDUITS, VALVES, AND FITTINGS

**Commercial Pipe.** As a result of the work of Nikuradse (11) and Colebrook (4) on the roughness problem, the pressure loss for fluids flowing in commercial pipes can be calculated from equation (47),  $\Delta p = 2fL\rho V^2/g_c D$ , using the effective roughness,  $k$ , from Table II (data of Moody and others) and the friction factor,  $f$ , from Figure 8.

TABLE II. Effective Roughness for Commercial Pipes.

Type of pipe	$k$ , ft.	$1/k$
Riveted steel.....	0.03-0.003	33-330
Concrete.....	0.01-0.001	100-1000
Wood stave.....	0.003-0.0006	330-1700
Cast iron.....	0.00085	1,200
Galvanized iron.....	0.0005	2,000
Asphalted cast iron.....	0.0004	2,500
Commercial steel or wrought iron.....	0.00015	6,700
Clean welded steel.....	0.000075	13,000
Drawn tubing.....	0.000005	200,000

Only the solid lines of Figure 8 should be used to obtain a friction factor, since the dotted lines represent regions of uncertainty or special cases as discussed in the section "Incompressible flow in pipes" (p. 626). It is also important to note that the friction factor,  $f$ , is the one familiar to chemical engineers and differs from the factor,  $f$ , used by mechanical engineers and the factor,  $\lambda$ , widely used in Europe.

**Valves and Fittings.** Friction losses in valves and fittings must be determined by experiment. Table III gives representative data for the coefficient,  $k'$ , for use in the equation:

$$h = k' V^2 / 2g \quad (107)$$

where  $h$  is the loss expressed in head of fluid flowing.

TABLE III. Loss Coefficients for Valves and Fittings.

Globe valve, open.....	10	45° elbow.....	0.5
Angle valve, open.....	5	90° standard elbow.....	1
Gate valve, open.....	0.2	90° medium-radius elbow.....	0.8
Gate valve, one-fourth closed.....	1.2	90° long-radius elbow.....	0.6
Gate valve, one-half closed.....	6	Standard tee.....	2
Gate valve, three-fourth closed.....	24	Close return bend.....	2.5

**Noncircular Cross Sections.** Experience has shown that equation (47) often gives a satisfactory solution for noncircular cross sections if a proper equivalent diameter is used. This diameter is four times the hydraulic radius:

$$D_e = 4 \frac{\text{cross-sectional area of flow}}{\text{wetted perimeter}} \quad (108)$$

For instance, for annular pipes:

$$D_e = 4 \frac{(\pi/4)(D_0^2 - D_i^2)}{\pi(D_0 + D_i)} = D_0 - D_i \quad (109)$$

Use of this equivalent diameter has been verified for values of  $D_i/D_0$  up to 0.3.

#### BEDS OF SOLIDS

**Fine Porous Bed.** Equation (108) may also be applied in the laminar flow of an incompressible fluid through a porous bed of finely divided solid particles. If the bed is treated in terms of an equivalent capillary, the pressure drop may be calculated from the Poiseuille equation (equation 21). A suitable equivalent diameter is obtained by multiplying and dividing equation (108) by the depth,  $L$ , of the bed:

$$D_e = 4 \frac{\text{free volume}}{\text{wetted surface}} = \frac{4SLv_f}{S_0\rho_s SL(1 - v_f)} = \frac{4v_f}{S_0\rho_s(1 - v_f)} \quad (110)$$

Since the actual velocity is the superficial velocity,  $V$ , divided by the fraction voids,  $v_f$ , substitution of equation (110) into equation (21) gives:

$$\frac{\Delta p}{L} = \frac{2\mu\rho_s^2 S_0^2 V}{g_c} \frac{(1 - v_f)^2}{v_f^3} \quad (111)$$

Equation (111) is equally useful for calculating pressure drop for a given flow, flow for a given pressure drop, or specific surface area from pressure drop and flow measurements.

**Fluidized Beds (13).** In beds of fluidized solids where  $v_f$  varies with the flow rate, the pressure drop is simply the weight of the bed divided by its cross-sectional area. Here the pressure drop due to friction is negligible, except with very viscous fluids.

**Packed Beds.** For laminar flow of a single fluid through beds packed with granular solids, Chilton and Colburn (1) give the equation:

$$\Delta p = 53\mu LVA_f/D_p^2 g_c \quad (112)$$

where  $A_f$  is a factor dependent on the ratio of particle diameter to tube diameter and has values of 0.9, 0.8, and 0.73 for diameter ratios of 0.05, 0.125, and 0.2, respectively.

For turbulent flow of a single fluid, there is no general correlation applicable to all types of packing. Leva and Grummer (7,8) have studied nearly all data available and have found an acceptable correlation for smooth cylinders and spheres and some irregular and rough shapes. The majority of the data for irregular particles, rings, and Berl saddles, however, are not correlated satisfactorily.

In the countercurrent flow of two fluids through a packed bed, the pressure drop of most engineering interest is the limiting pressure drop at flooding conditions. Zenz (14) has compared the available data and finds that this pressure drop, independent of liquid and gas rates, is a function of packing characteristics and liquid viscosity and density. Although Zenz gives no general correlation, his organization of the empirical data on Raschig rings, Berl saddles, and spheres represents the most useful presentation so far available on gas-liquid systems under flooding conditions.

## OTHER APPARATUS

**Tube Banks.** Equations for calculating the pressure drop in fluids flowing across banks of tubes are given by Chilton and Genereaux (2), Jakob (6), McAdams (9), and Perry (12).

**Bubble-Plates.** The method of Dauphine (3,5) appears to be the best currently available for calculating the pressure drop through operating bubble-cap plates in distillation columns. This method, which is rather detailed, obtains the summation of the resistances imposed by the dynamic liquid head above the slots and the individual friction losses through the various parts of the bubble-cap assembly.

## Nomenclature

$A$	a constant; $A \equiv Re^* \xi x'$ for smooth pipes	Dimensionless
$B$	reference region of fluid volume	$L^3$
$C_c$	contraction coefficient, ratio of two areas through which the stream of fluid flows	Dimensionless
$c$	a constant	Dimensionless
$c_p$	specific heat at constant pressure	$FL/MT$
$D$	diameter of pipe	$L$
$D_e$	equivalent diameter of noncircular pipe	$L$
$E$	total energy per unit mass	$FL/M$
$F$	force	$F$
$f$	friction factor	Dimensionless
$\Delta F$	a dissipation term for energy	$FL/M$
$f'$	frequency of sound wave	$1/t$
$G$	mass velocity	$M/L^2t$
$g$	acceleration of gravity	$L/t^2$
$g_0$	proportionality factor in Newton's second law; $g_0 \equiv \frac{1}{ F } \left  \frac{d(mv)}{dt} \right $	$ML/Ft^2$
$H$	enthalpy per unit mass	$FL/M$
$K$	a constant; $K \equiv -g_c e(\tau)/(dv_x/dr)$	$M/Lt$
$k$	roughness parameter	$L$
$L$	length of pipe or packed bed	$L$
$l$	mixing length	$L$
$m$	mass	$M$
$N$	net rate of transport through boundary other than by mass flow	Undefined
$n$	amount per unit volume	Undefined
$p$	pressure	$F/L^2$
$\Delta p^*$	$\Delta p + \rho(g/g_c)\Delta z$	$F/L^2$
$Q$	heat input per unit mass	$FL/M$
$Q'$	rate of flow of heat into reference region	$FL/t$
$q$	rate of flow of heat per unit area	$F/Lt$
$R$	rate of generation in reference region	Undefined
$R_i$	correlation coefficient for fluctuations in velocity	Dimensionless
$r$	radial coordinate	$L$
$r_0$	radius of pipe	$L$
$Re$	Reynolds number; $Re \equiv D\rho v/\mu$	Dimensionless
$Re^*$	$Re^* \equiv V_z^* r_0/\nu$	Dimensionless
$S$	surface of reference region	$L^2$
$S_0$	surface solid per unit mass	$L^2/M$
$t$	time	$t$
$T$	temperature	$T$
$U$	internal energy per unit mass	$FL/M$
$u, v$	axial and radial components of velocity	$L/t$
$u, v, w$	$x, y,$ and $z$ components of velocity	$L/t$

$u', v'$	fluctuations in axial and radial components of velocity	$L/t$
$V$	volumetric average velocity	$L/t$
$V_x$	$x$ component of velocity	$L/t$
$V^*$	friction velocity; $V^* \equiv \sqrt{g\epsilon r_0/\rho}$	$L/t$
$v_f$	fraction void	Dimensionless
$W_s$	rate of shear work per unit area	$F/Lt$
$w_s$	work input per unit mass	$FL/M$
$W'_s$	rate of doing shear work on surface of reference region	$FL/t$
$X$	$x$ component of body force per unit mass	$F/M$
$x$	axial coordinate	$L$
$y_s$	$y_s \equiv y/l$	Dimensionless
$x, y, z$	rectangular Cartesian coordinates	$L$
$z$	height	$L$
$\alpha$	ratio of the cube of the average velocity to the average of the cube of the velocity	Dimensionless
$\beta$	ratio of the square of the average velocity to the average of the square of the velocity	Dimensionless
$\gamma$	angle between axis of pipe and a horizontal plane	Dimensionless
$\delta$	thickness of the laminar sublayer	$L$
$\epsilon$	function of $\tau$ , proportional to $dw_x/dr$	$F/L^2$
$\theta$	angle between flow and outward normal to surface of reference region	Dimensionless
$\kappa$	von Kármán constant; $\kappa \equiv -l \frac{d^2v_x}{dy^2} \bigg/ \frac{dv_x}{dy}$	Dimensionless
$\mu$	viscosity	$M/Lt$
$\nu$	kinematic viscosity; $\nu \equiv \mu/\rho$	$L^2/t$
$\xi$	a coordinate; $\xi \equiv 1 - (r/r_0)$	Dimensionless
$\rho$	density	$M/L^3$
$\rho_s$	density of solid	$M/L^3$
$\tau$	shear stress	$F/L^2$
$\tau_t$	turbulent shear stress	$F/L^2$
$\phi$	velocity potential	$L^2/t$
$\chi$	$V_x/V_x^*$ , a function of $Re^*\xi$ and roughness	Dimensionless
$\psi$	$(V_{x, \max} - V_x)/V_x^*$	Dimensionless
$\omega$	$V_x/V_x^*$ , a function of $Re^*$ , $\xi$ , and roughness	Dimensionless
$\Delta$	difference operator	Dimensionless
$\Omega$	$\Omega(Re^*) \equiv \omega(Re^*, l)$ for smooth pipes	Dimensionless

Note: a bar indicates the average of the quantity under the bar, thus  $\overline{(v')^2}$ .

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## FLOW MEASUREMENT

The measurement of fluid flow, as here considered, includes description of the devices and methods commonly used to determine the total quantity of flow over a period of time or the rate of flow at an instant of time, with particular emphasis on the applications most useful in the process industries. The theoretical basis of fluid flow is discussed under the section on "Principles" (see p. 614).

It is beyond the scope of this article even to list, much less describe, the hundreds of fluid meters which are commercially available, hence descriptions are confined to typical devices grouped according to the primary measurement used to determine flow. These primary measurements include: (1) fluid discharge, (2) fluid force, (3) fluid level, (4) variable area, (5) differential pressure, (6) thermal effects, and (7) material balance.

## Measurement of Discharge

The direct measurement of the quantity of fluid discharged over a period of time is widely used as a means for calibrating flowmeters of all types. The method simply involves flow over a measured time into gravimetric or volumetric measuring tanks with suitable correction for errors in starting and stopping the flow. With gases and volatile liquids, the actual measurement is made with a second fluid, usually a liquid such as water or mercury, in which the primary fluid has negligible solubility and which is displaced from the flow tank by the primary fluid. Suitable corrections must, of course, be made for the volatilization of the confining liquid and for reduction to standard conditions of temperature and pressure.

A number of devices both gravimetric and volumetric utilize the principle of direct measurement by alternately filling and dumping, and recording the number of tiltings. These are particularly useful with dirty liquids or liquids carrying suspended solids on which other meters are inoperable. Akin to the tilting meters, are the *revolving drum meters*. These use a drum divided into sections into which the fluid successively flows to cause a shift in the center of gravity and hence a rotation of the drum. The drum is connected to a revolution counter that registers the flow. Figure 1 shows a wet-gas meter of this type. The sealing liquid, usually water or oil, covers all ports so that the gas entering the hub is directed to compartment A. A shift in the center of gravity causes the drum to rotate in the direction of the arrow, sealing port *a* and opening port *b* to compartment B. In this manner rotation continues during gas flow. In this meter the liquid level must be maintained without disturbance, hence the meter must be level and accurately filled, and gas surges must be avoided. With careful adjustment the error of flow measurement is between 0.5 and 1%. This meter has a very low pressure loss and is well adapted to measurement of low and inter-

mittent flows, but it can be used only with low line pressures (atmospheric to 3 p.s.i.g.) and for clean and noncorrosive gases.

The drum meter is also available commercially for liquids. The operation with liquid flow may be seen by inverting Figure 1 and regarding the unshaded portion as the area occupied by liquid. In liquid service, operation is at substantially atmospheric pressure with free gravity discharge and with about 18 in. loss in static head. The error of measurement is larger with liquids, ranging from 2 to 3% under favorable conditions.

**Displacement Meters.** Mechanical meters operating on the principle of positive displacement of the flowing fluid are legion. Nearly every type of positive displacement pump has been adapted to fluid metering. The principal types include the rotary disk, the double-acting piston, the rotary piston, the oscillating piston, the revolving gear, the cycloidal gear, the paired bellows, and the diaphragm. Although displacement meters are widely used in metering fluids for sale, such as the rotary-disk meter for household water and the paired diaphragm meter for domestic fuel gas, these devices have found only limited application in the process industries.

### Measurement by Fluid Force

A number of devices for measuring fluid velocity depend on fluid force. One group comprises the spring-loaded vane or cup in which the velocity is related to the displacement or tension on the spring. Other devices are designed to translate fluid velocity into speed of rotation. In this group are the meteorological *anemometers* of the cup or vane type and the hydraulic *current meters* such as the screw or propeller used in streams and channels. All of these devices are relatively inaccurate and have little application in process plants.

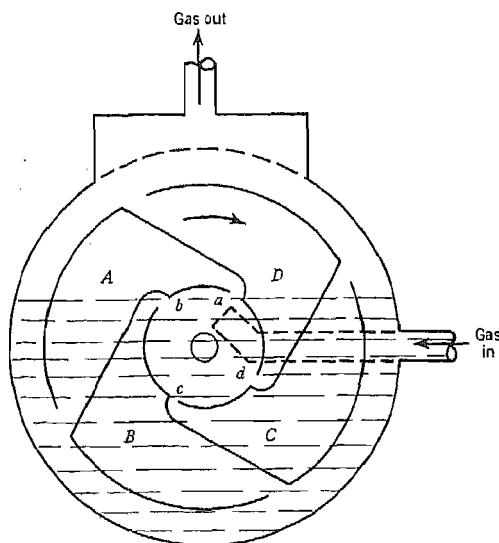


Fig. 1. Wet-gas meter.

### Measurement by Fluid Level

**Orifice in Gage Tank.** Measurement in a gage tank of the fluid level or potential head required to discharge the flow through a free-flowing orifice in the bottom of the tank has been used by hydraulic engineers. Since this method is limited to fluids which can be exposed to the atmosphere (such as water) and is attended by all the difficulties and necessary precautions involved in using an orifice meter in a pipe-run, it has little application in the process industries.

**Weirs.** The weir, a dam in a horizontal open channel over which the flow is discharged, is a simple and widely used means for estimating rate of flow. Commonly, the weir plate or crest is square-edged and of relatively thin section although broad crested weirs are also used. A weir is *contracted* if the width of the discharged sheet of fluid is less than the length of the crest. When the weir is constructed so as to avoid



contraction, the weir is *suppressed*. Weirs are also known by the shape of the opening formed by the sides and crest, as *rectangular*, *triangular* (V-notch), or *trapezoidal*.

*Weir Formulas.* Schoder and Turner give a review of formulas for calculating the discharge over weirs, and Addison presents an account of the practical difficulties in the application of weirs (1,9,10).

A number of equations commonly used for sharp-edged weirs are given below. In these equations:  $q$  = rate of discharge, cu.ft./sec.;  $C$ ,  $c$ ,  $c'$  = coefficients;  $L$  = length of weir crest, ft.;  $h$  = upstream static head above crest, ft.;  $V$  = upstream average velocity, ft./sec.;  $g$  = local acceleration of gravity, ft./sec.<sup>2</sup>; and  $\alpha$  = included angle of a V-notch.

The general equation for the discharge over a sharp-edged rectangular weir is:

$$q = CL(2g)^{1/2}h^{3/2}$$

The Francis formula for a suppressed weir is:

$$q = 3.33L \left[ \left( h + \frac{V^2}{2g} \right)^{3/2} - \left( \frac{V^2}{2g} \right)^{3/2} \right]$$

and for a contracted weir is:

$$q = 3.33 [L - 0.2h] \left[ \left( h + \frac{V^2}{2g} \right)^{3/2} - \left( \frac{V^2}{2g} \right)^{3/2} \right]$$

Discharge over a triangular weir is given by:

$$q = c \frac{8}{15} \left( \tan \frac{\alpha}{2} \right) (2g)^{1/2} h^{5/2}$$

or since  $c$  varies to some extent with head, by:

$$q = c'h^{2.48}$$

where  $c' = 2.48$  for  $90^\circ$  included angle, 1.24 for  $53^\circ 8'$  included angle, and 0.62 for  $27^\circ$  included angle.

The Cipolletti trapezoidal weir is constructed with outwardly sloping sides forming an angle of  $166^\circ$  with the horizontal crest. As a fully contracted, sharp-edged weir the discharge is given by:

$$q = 3.37L \left[ \left( h + \frac{V^2}{2g} \right)^{3/2} - \left( \frac{V^2}{2g} \right)^{3/2} \right]$$

The apparent simplicity of the weir is a delusion in actual practice, since appreciable errors are introduced by: (1) slight rounding of the presumed sharp-edged crest, (2) roughness of the upstream bed or weir partition, (3) a clinging rather than a free-springing nappe, (4) eddies, swirls, or surges in the upstream velocity distribution. All of these sources of error contribute to an actual discharge larger than the calculated discharge. Under research conditions the total error may be kept under 2%, but in normal engineering practice the error is much larger, perhaps as much as 10–20% in a bubble-column, for example.

## Measurement by Variable Area

Meters operating on the principle of variable area incorporate an adjustable constriction in the path of flow which may be varied so as to maintain a constant differential pressure. Meters of this type have been offered commercially in the form of gate valves, multiple orifices, adjustable slots, iris diaphragms, and adjustable segmental orifices. None of these devices, however, has attained the general acceptance accorded the *rotameter*, which is now the outstanding example among area meters.

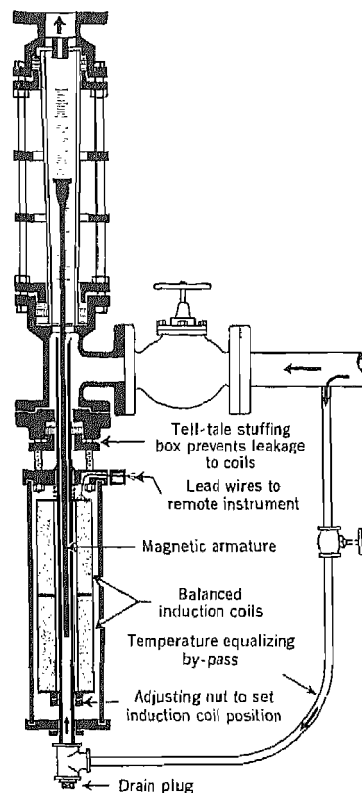
**Rotameters.** The rotameter is a tapered vertical tube containing a free plummet or "float" (Fig. 2). Fluid entering the lower, small end of the tube lifts the plummet until the annular area between plummet and tapered tube provides a dynamic force balance around the plummet. The level of the plummet or "float" indicates the rate of flow.

Rotameters are supplied with glass and metal tubes to meet a variety of service conditions in metering clean liquids and gases. Nearly all corrosive conditions can be provided for. Temperatures up to 800°F. and pressures up to 5000 p.s.i. can be accommodated by rotameters commercially available. Standardized interchangeable floats and precision-bore tubes are supplied to provide capacities from 0.15 cu.cm. to 1000 gal./min. for water, or from 5 cu.cm. to 1000 standard cu.ft./min. for air. Rotameters can be used for manual or automatic control of flow, and can be adapted to indicating and recording instruments. Figure 2 shows a rotameter with an electric impedance bridge for transmitting readings to a remote secondary instrument.

Reliability of calibration, simplicity of installation, and convenience in operation have contributed to the growing popularity of the rotameter. With the small and moderate flow rates encountered in laboratory, pilot-plant, and many commercial operations, the rotameter has become the preferred device for measurement of flow. For precise metering, a rotameter calibrated with the fluid which is to be metered is unsurpassed. With very large flow rates, especially for gases, the cost and bulk of the rotameter as compared to an orifice meter are important disadvantages.

The flow rate indicated by a rotameter is a function of the annular area, the float diameter, weight, and shape, and the fluid density and viscosity. The general equation of the rotameter in consistent units, for volumetric rate of flow, is:

$$q = CA_x \left[ \frac{2gv_f(\rho_f - \rho_w)}{A_f \rho_w} \right]^{1/2}$$



Courtesy Fischer & Porter Company.

Fig. 2. Rotameter with electric transmitter.

and for weight rate of flow is:

$$w = CA_w \left[ \frac{2gv_f(\rho_f - \rho_w)\rho_w}{A_f} \right]^{1/2}$$

$q$  = volumetric rate of flow, cu.ft./sec.;  $w$  = weight rate of flow, (lb.-mass/sec.)( $g/g_c$ );  $A_w$  = area of minimum section of annulus, sq.ft.;  $A_f$  = area of maximum section of float, sq.ft.;  $\rho_f$  = weight density of float, (lb.-mass/cu.ft.)( $g/g_c$ );  $\rho_w$  = weight density of fluid, (lb.-mass/cu.ft.)( $g/g_c$ );  $v_f$  = volume of float, cu.ft.;  $g$  = acceleration of gravity, ft./sec.<sup>2</sup>, nominally 32.17;  $g_c$  = conversion factor for mass and force units = 32.17; and  $C$  = coefficient of discharge.

Inspection of the term  $[\rho_w(\rho_f - \rho_w)]^{1/2}$  in the equation for weight rate of flow shows that it may be made insensitive to normal fluctuations in fluid density if the float density is twice the mean density of the fluid to be metered. The coefficient of discharge,  $C$ , is a function of the Reynolds number at the annulus and the shape of the float. It has been shown that floats can be designed so that the coefficient becomes relatively insensitive to changes in Reynolds number, and hence the effect of changes in viscosity can be largely nullified (6). Viscosity-insensitive floats are illustrated by

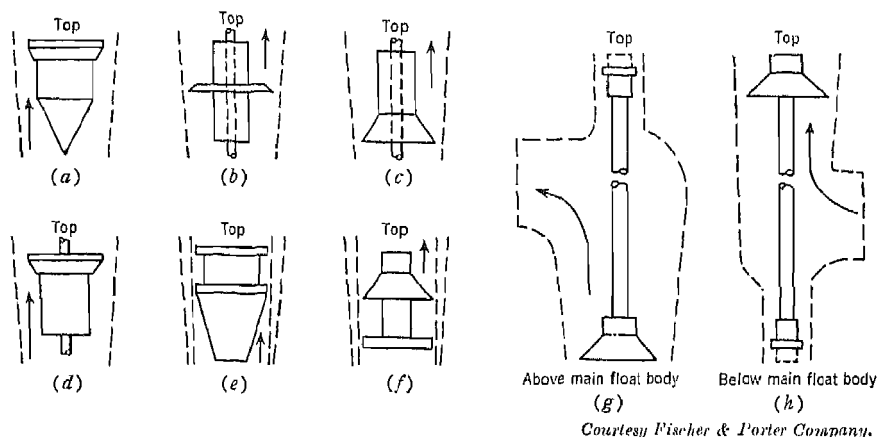


Fig. 3. Typical rotameter floats.

Figure 3 (b, c, f, g, and h). Extended discussions of the theory and calibration of rotameters may be found by reference to Schoenborn and Colburn (11), Fisher, Bleekman, and Lipstein (6), and Martin (8).

### Measurement by Differential Pressure

The most widely used devices for measuring the flow of fluids are those which utilize a fixed constriction in the path of flow to produce a difference in pressure between upstream and downstream points. Application of this differential pressure in Bernoulli's equation (see p. 635) leads to a formal expression for the rate of flow. *Nozzles*, *Venturi tubes*, and *orifices* are the principal forms of constrictions used. A nozzle is a constriction, usually circular, flared on the upstream side to simulate the streamlines of the contracting flow. A Venturi tube consists of a standardized conical nozzle and a more gradually expanding downstream cone to recover most of the fluid

energy otherwise lost with sudden expansion. The metering orifice has been standardized in the United States as a centered, circular, square-edged opening in a thin plate. Other configurations such as square, segmental, and eccentric circular openings have been largely abandoned.

**Flow Equations.** The American Society of Mechanical Engineers Special Research Committee on Fluid Meters recommends for horizontal nozzles, Venturi tubes, and orifices a practical equation for weight rate of discharge of gases or liquids:

$$w = q_1 \rho_1 = CYA_2 \left[ \frac{2g_c(p_1 - p_2)\rho_1}{1 - \beta^4} \right]^{1/2}$$

where  $A_2$  = cross-sectional area of discharge opening, sq.ft.;  $C$  = coefficient of discharge;  $g_c = 32.17$  (lb.-mass)(ft.)/(lb.-force)(sec.<sup>2</sup>);  $p_1$  and  $p_2$  = pressures at upstream and downstream static-pressure taps, lb.-force/sq.ft.;  $q_1$  = volumetric rate of discharge measured at upstream pressure and temperature, cu.ft./sec.;  $w$  = weight rate of discharge, lb.-mass/sec.;  $Y$  = expansion factor for gases (for liquids,  $Y = 1$ );  $\beta^2$  = ratio of cross section of constriction to that of upstream channel (for circular sections,  $\beta = D_2/D_1$ ); and  $\rho_1$  = density at upstream temperature and pressure, lb.-mass/cu.ft. For standard square-edged orifices, the value of  $Y$  is given by:

$$Y = 1 - \left( \frac{p_1 - p_2}{kp_1} \right) (0.41 + 0.35\beta^4)$$

where  $k$  is the ratio of specific heats at constant pressure and constant volume. For nozzles and Venturi tubes, the value of  $Y$  is a complex function of the ratio of specific heats, the ratio of pressures, and the ratio of areas, given approximately by:

$$Y = 1 - \left( \frac{p_1 - p_2}{kp_1} \right) (0.8 + 0.8\beta^4)$$

For precise values of  $Y$ , standard tabulations should be consulted (3).

Values for the discharge coefficient,  $C$ , are to be found in engineering handbooks and trade publications of meter manufacturers (often presented as  $K = CY$ ), but the reader is advised to consult the original sources for precise values, since the coefficients differ according to location of the pressure taps and are valid only with a corresponding equation of flow (2,3).

**Nozzles.** The flow nozzle is usually designed so that there is no vena contracta, that is, the issuing jet is of the same diameter as the throat. Although nozzles have not been completely standardized, a large amount of data has been obtained with the "long radius" or elliptical nozzle which is extensively used in Europe. Folsom presents data on this type of nozzle (7). The overall pressure loss for a nozzle is not as well known as for an orifice but appears to be of the same order of magnitude, since both devices discharge into a "stagnant" downstream fluid so that the kinetic energy is largely dissipated in turbulent friction. The equation for loss on sudden expansion is usually the basis for calculating pressure loss in a nozzle. The flow nozzle has not been highly regarded in the United States because it requires nearly as long a run of straight pipe as the Venturi tube, without the advantage of high pressure recovery, and yet produces a smaller differential pressure than the orifice.

**Venturi Tube.** The standard Venturi tube consists of: (1) a cylindrical inlet of

the same diameter as the supply line; (2) a frustum of a cone with vertex angle of 25–30°; (3) a cylindrical throat of  $\frac{1}{4}$ – $\frac{1}{2}$  the inlet diameter, and length about  $\frac{1}{2}$  the inlet diameter; and (4) an expanding conical section increasing toward the discharge pipe at a constant angle of 7°. The coefficient of discharge is very high, about 0.98 for Reynolds numbers exceeding 10,000, and the overall pressure loss is low, usually from 10 to 20% of the differential pressure. The Venturi tube is a rugged precision meter, but suffers from the very considerable disadvantages of high cost and large space requirement.

**Orifice Meters.** In order that one installation may reproduce the results of another within a tolerable error, orifice installations have been rigorously standardized, largely as the result of work by the A.S.M.E. Special Research Committee on Fluid

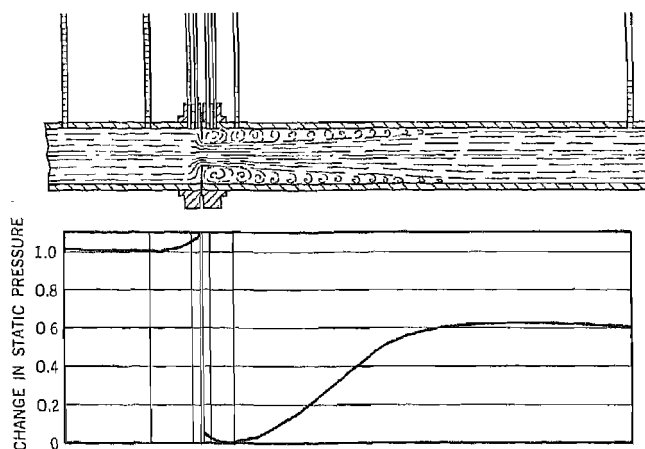


Fig. 4. Location of common pressure taps and profile of static pressure for a square-edged orifice (3).

Meters and the Joint A.G.A.-A.S.M.E. Committee on Orifice Coefficients. Their publications should be consulted before making an orifice installation, and no uncalibrated orifice should be relied upon unless it conforms in detail to their standards (2,3).

For the calculated discharge of an orifice to be acceptable, it is essential that the orifice plate and conduit meet sharply at right angles; the areas of pipe and opening be accurately known; the plate thickness be less than  $\frac{1}{30}$  of the pipe diameter,  $\frac{1}{8}$  of the orifice diameter, or  $\frac{1}{4}$  of the distance from the pipe wall to the edge of the opening; the upstream face of the plate be a smooth plane; and the pressure taps be accurately fitted. Relatively slight rounding of the upstream edge, corrosion, or fouling seriously affect the calibration. Abnormal velocity distribution such as swirling or helical flow and pulsations make the reading undependable, hence standard pipe-runs and straightening vanes are essential. Figure 4 shows the pressures above and below a thin-plate orifice.

For a completely standard orifice meter, newly installed and operating on clean, noncorrosive fluids, an accuracy of about 2% may be expected, exclusive of the additional error involved in reading or transmitting the differential pressure. For precision work, calibration of the complete installation with the fluid to be metered is indispensable.

### Measurement by Thermal Effects

The addition or removal of heat within the flowing fluid and application of a heat balance to calculate the flow is the basis for a flowmeter. If the pressure drop and temperature rise are small, the equation below is applicable to both liquids and gases:

$$w = \frac{Q}{c_p(t_2 - t_1)}$$

where  $w$  = weight rate of flow, lb.-mass/sec.;  $Q$  = heat supplied, B.t.u./sec.;  $c_p$  = specific heat of fluid at constant pressure, B.t.u./(lb.-mass)(°F.); and  $t_2 - t_1$  = rise in temperature of the fluid, °F.

In the *Thomas electric flowmeter*, heat is supplied to the fluid by an electric heating coil wound on a grid in a cross section of the duct, and resistance thermometers are placed before and after the heater. The temperature rise is kept constant by adjusting the direct current to the heater, and the flow rate is calibrated in proportion to the reading on a wattmeter in the heating circuit. The accuracy of such an instrument is dependent largely upon the accuracy of the temperature measurement and control.

**The Hot-Wire Anemometer.** The hot-wire anemometer is a useful tool for exploring the local velocity distribution in a duct or channel. As the name indicates, it is principally used for gases although it can be adapted for liquids. In principle, the hot-wire anemometer is a fine wire, heated electrically and exposed to the fluid so that change in fluid velocity cools the wire and alters its electrical resistance. If, for instance, constant current is supplied to the wire, fluctuations in fluid velocity, by changing the electrical resistance, produce corresponding fluctuations in the voltage drop across the wire, which becomes the measure of the velocity fluctuations. The theory of the hot-wire anemometer is given briefly by Dryden (5) and thoroughly by Corrsin (4).

### Measurement by Material Balance

If an extraneous soluble substance is metered into a fluid stream, and upstream and downstream samples of the fluid are analyzed for the added substance, the rate of flow can be calculated by a material balance. Thus:

$$qx_0 + E = (q + E)x_e \quad \text{or} \quad q = E(1 - x_e)/(x_e - x_0)$$

where  $q$  = rate of flow upstream,  $x_0$  = concentration of additive upstream,  $E$  = rate of additive metered in, and  $x_e$  = concentration of additive downstream.

Where accurately measurable changes in a physical property, such as refractive index or thermal or electrical conductivity, are produced by a small quantity of additive, measurement of the physical property may replace the chemical analyses and thus provide the basis for a continuous flowmeter. If means are provided to assure good mixing, the method of material balance may be made to produce any desired accuracy by adjusting the rate of additive input to the precision of the analysis. Consequently, this method is very useful for calibrating other types of meters.

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MOTT SOUDERS, JR.

## FLUID TRANSPORTATION

In the chemical industries, the fluids which are transported range from gases through liquids of all viscosities to slurries and sludges. Conditions encountered include a wide variety of corrosive situations, pressures up to several thousand pounds per square inch, and temperatures up to 1000°F. Hence, apparatus used to transfer fluids has been made of nearly every material that could be machined, cast, or molded.

See also *Pressure technique*; *Vacuum technique*.

### Pumps

Pumps may be classified according to the materials of construction, the driving means, the mechanism of the pump, or the services for which they are intended. For the discussion which follows, pumps have been divided into three groups: (1) those which raise the elevation, (2) those which increase the pressure, and (3) those which increase the kinetic energy of the fluid.

#### PUMPS WHICH INCREASE THE ELEVATION

**Elevators and Conveyors.** In instances where the service is infrequent, where no other facilities exist, where the quantities are not large, or where the liquid is extremely difficult to handle due to corrosiveness or abrasiveness, elevators and conveyors may be the only feasible means or the most practical and economical method for raising or transporting the liquid. The means for elevating a liquid by conveying devices include most of the primitive machine elements: the lever (*well sweep*), the wheel (*water wheel*), the inclined plane (*railroad tank car* and *bucket conveyors*), the pulley (*elevator hoists*), the screw (*Archimedes' screw*), and the wedge (the locomotive *water scoop*).

**Density Pumps.** Two interconnected columns of liquid will not have the same total head at corresponding elevations other than that of the connection between them, if the densities of the liquids in the two columns are different. If means can be found for maintaining a difference in density in the two interconnected columns of liquid, the resulting difference in head may be utilized to cause flow in the circuit, thus producing a *density pump*.

If one column is heated, or the other column is cooled, or both, and the head

differential is utilized to cause flow in the circuit, the system is referred to as a *thermal-convection* or *free-convection system*. If one column is heated to the boiling point, so that the effective density is that of the mixture of liquid and its vapor, a larger head differential is established. The utilization of the boiling action is referred to as a *thermo-syphon* system. The thermo-syphon is normally employed where vaporization of a liquid is simultaneously required for purposes apart from circulation of the liquid, as in a steam generator or distillation column reboiler. The domestic coffee percolator employs the thermo-syphon system to pump hot water over the coffee grounds.

The same effect as in the thermo-syphon system may be realized by the injection of air or gas under pressure into the column of liquid. The *air* or *gas lift* is useful in water or oil wells in cases where the liquid in the well is at a level too far beneath the surface for barometric pressure head to elevate the liquid to a pump at ground level. Practical pumping heads range up to the order of a thousand feet. Typical head of the dense liquid column above the point at which the gas is injected into the low-density column is one-third of the head of the latter column.

The differential density principle is also utilized for transfer of a liquid by total vaporization at one point in a circuit, followed by condensation at some other location. The circulation of steam and condensate in a steam heating system without the intervention of a pumping machine is an instance of the technical application of the density-differential system.

#### PUMPS WHICH INCREASE PRESSURE

**Pistonless Pumps.** Liquids may be transported from one vessel to another, through piping of various lengths, under the influence of the pressure of an auxiliary fluid usually immiscible with the liquid transported. Air or gas may be employed (or water, to displace oil), for example. Heating a volatile liquid in the original vessel, or cooling the vapor in the receiving vessel, or both, results in a "pumping" pressure differential which will cause the desired flow. In this case, the liquid transported is displaced by its own vapor.

When the displacement chamber is made small compared to the supply or receiving vessel, and is arranged for automatic and cyclic operation, the device is called a *pistonless pump*. Any fluid appropriate for a blow-case operation is suitable for a pistonless pump, providing that a supply is maintained under sufficient pressure, and that the fluid is expendable or easily recoverable after use. One arrangement uses steam for the motive fluid. The pressure discharges the pumped fluid, and the reduction in pressure which is induced cyclically by injection of the cold liquid, or water, allows the pumped fluid to refill the chamber from the supply vessel. This device is known as the *pulsometer*. It is a low-cost device, requires little operating attention, and achieves a discharge pressure close to that of the supply steam.

**Reciprocating pumps**, which employ a plunger, piston, or diaphragm to displace the pumped fluid, provide the most positive means for maintaining a constant volume of flow against a variable discharge head. The ability to handle compressible fluids dictates their selection when operating with variable suction conditions where air or gas is apt to enter the pump suction to an extent that would cause a centrifugal pump to cease pumping. The liquid velocities in a reciprocating pump are usually low; this makes them particularly suitable for viscous liquids. Reciprocating pumps may be designed to produce the highest heads, and to handle the smallest flows that may be required.



The cost of reciprocating pumps of standard design is moderate to low, especially low when direct drive by steam power is contemplated and the drive cost included with the pump. Specially designed pumps for exceptionally high pressure or small flows are more readily available as reciprocating pumps than any other type of pump. The normal life of a reciprocating pump is long, maintenance and repair are fairly simple, hence reliability is good. Continuous maintenance is required for good perform-

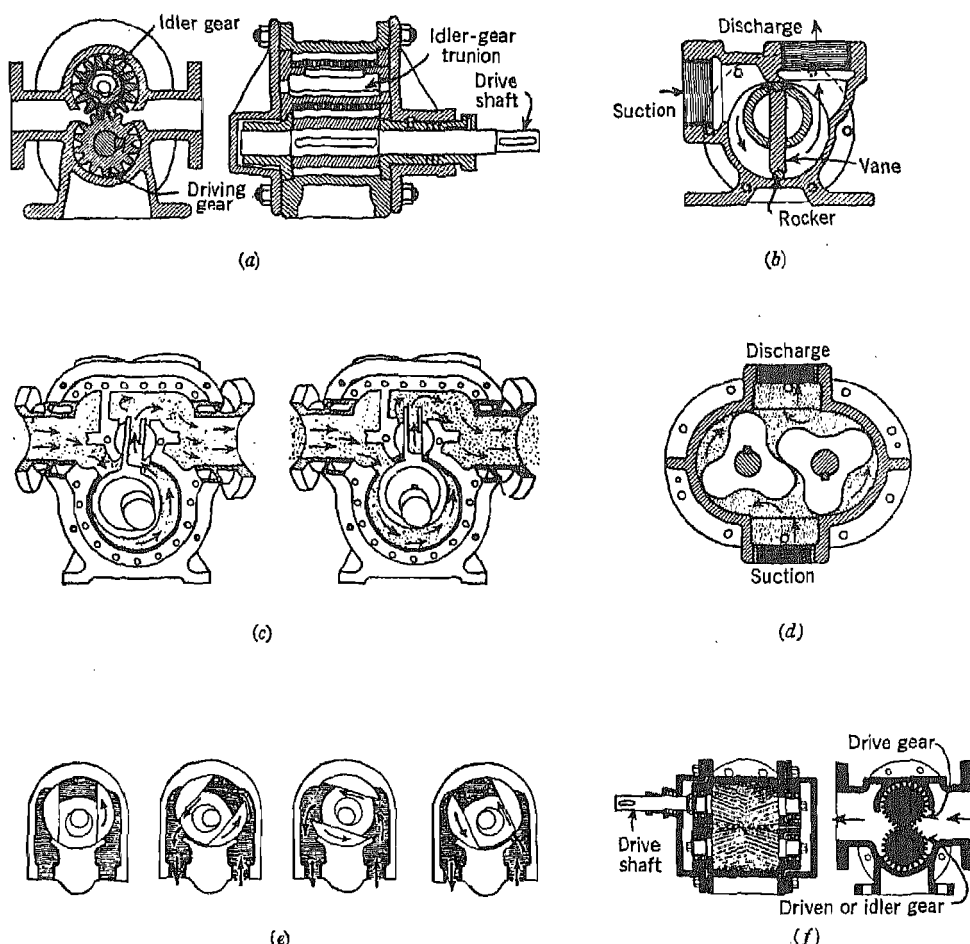


Fig. 1. Rotary displacement pumps: (a) spur gear, (b) rotary plunger, (c) rotary piston, (d) three-lobe rotary, (e) single-vane rotary, (f) herringbone gear.

ance, however, and the flow is intrinsically pulsating. For electric motor drive at constant speed, a rotary or centrifugal pump is to be preferred. Steam-driven reciprocating pumps are extremely valuable for stand-by service where electric power failures must be contemplated.

**Rotary displacement pumps** exist in rich variety. Some of the better-known types are shown in Figure 1, and include meshing spur gears, meshing helical or herringbone gears, meshing lobes, eccentric rotor and vanes, gyratory rotor with vane, and the rotary piston. All of these pumps employ the following operating cycle: (1)

space opens at the inlet to receive liquid, (2) liquid is entrapped and conveyed to the outlet, (3) space closes at the outlet forcing the liquid out.

Rotary pumps are suitable for liquids which are clean, more viscous than water, and have lubricating characteristics; they are particularly useful for supplying a fixed rate of flow without auxiliary controls. In the simpler types these pumps are relatively small and low in initial cost. Nearly all types produce a flow that is freer from pulsations than that from a reciprocating pump, and a more constant volume against variable head than that from a centrifugal pump. External timing-gears and bearings are employed to control the clearance of mating parts and to reduce rotor wear in pumps designed for handling nonviscous or nonlubricating liquids at appreciable pumping heads. Rubber rotors, vanes, or liners are useful for the anti-friction and abrasion resistance qualities of rubber when pumping dirty water and abrasive slurries. Several types are inherently designed or easily adapted for variable-displacement operation of the pumping element, which obviates the necessity for an adjustable-speed drive or external by-pass controls in order to secure any desired flow or pressure within the capacity of the pump.

For pumping very viscous liquids, it is usually necessary to operate a rotary displacement pump at reduced speed in order to allow time for the liquid to flow into the spaces where it is entrapped, and to flow out as fast as it is displaced, without the development of excessive local pressure, that is, between gear teeth. Herringbone-gear wheels, and other special provisions, often permit a pump to be operated at much higher speeds with liquid of a given viscosity before it becomes strained by excessive pressure or loses capacity due to cavitation. The small size and compact arrangement of most types of rotary displacement pumps facilitate the construction of heated jackets, which enable the pump to handle extremely viscous liquids or molten solids without risk of freezing of the rotors. Rotary displacement pumps, like reciprocating pumps, have the ability to handle gases with the liquid without loss of prime. This enables a rotary pump to remove gas from the suction line and permit liquid to flow to the pump under barometric pressure, even when the pump is located above the liquid level.

**Slip and Volumetric Efficiency.** Displacement-type pumps do not discharge a volume of liquid equal to the volume displaced by the solid element, because of internal leakage of the liquid past valves, pistons, or rotors. The ratio of the volume of liquid discharged to the volume displaced by the pump element is called the *volumetric efficiency*. The amount of internal leakage, called the *slip*, results in a decrease in the hydraulic efficiency of the pump.

When the pumping pressure increases, the internal leakage or slip of the pump increases. At low pumping rate or high pressure, the slip of a pump may increase until it equals or exceeds the displacement of the pumping element, especially when pumping a liquid of low viscosity. When pumping a compressible fluid, the volumetric efficiency of the pump is decreased due to the decrease in volume of the fluid during pumping. This effect increases the apparent slip of the pump and is particularly important in gas compressors. When reciprocating pumps are employed in handling dirty, abrasive, or corrosive liquids, or when the pump is used to meter a liquid, the internal leakage must be kept to a minimum. One means for reducing slip, due to valve leakage, is to employ two or more sets of suction and discharge valves through which the liquid must flow successively. If the valves do not often fail to close, the coincidental failure of both valves during the same stroke is unlikely.

## PUMPS WHICH INCREASE KINETIC ENERGY

**Impact and Momentum Pumps.** An *ejector* consists of a nozzle for converting the pressure head of a working fluid into a high-velocity stream, a mixing chamber for entraining the fluid to be pumped, and a diffuser for converting the velocity head of the mixture into a pressure head. The initial pressure of the working fluid is commonly two or more times the desired discharge pressure of the mixture, which in turn is commonly as high as four to six times the pressure in the mixing chamber. Since momentum is conserved, the momentum of the mixture is the same as that of the working fluid before mixing with the entrained fluid. The mechanical efficiency of ejectors is very poor, but the apparatus is simple and therefore economical in special cases. Steam and water are common working fluids in ejectors, but any available fluid under pressure is suitable. Ejectors are particularly appropriate for the following uses: (1) where use is infrequent and the operating period is short, such as priming a centrifugal pump; (2) where mixing of the working fluid with the pump fluid is desired, as in

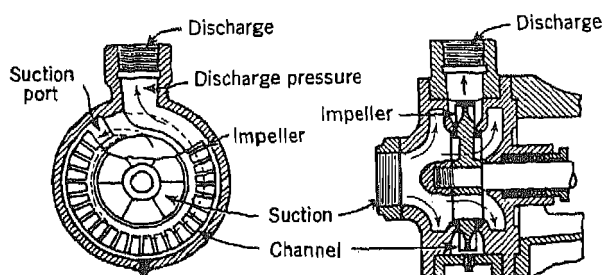


Fig. 2. Turbine pump.

pumping cold water and heating with steam simultaneously; (3) where the fluid is costly to handle by more efficient means, fluids such as slurries or those containing abrasive solids; (4) as deep-well pumps where barometric pressure is insufficient to lift water to a pump located at ground level; and (5) to exhaust noncondensable gases from apparatus maintained under vacuum.

The *hydraulic ram* is a pump which utilizes momentum of a flowing liquid stream to force a small quantity of the liquid into a branch pipe by means of sudden interruption of the main flow. The amount of liquid which can be so pumped is limited to some fraction of the main-stream rate, since the momentum of the pumped fraction is substantially less than the available momentum. The pumping efficiency is low.

**Turbine Pumps.** Figure 2 shows the typical arrangement of vanes for a turbine pump. The impeller consists of a disk with shallow radial vanes located at the periphery and running in an annular channel formed by the case. The cross-sectional area of the casing channel is large compared to the projected area of the vanes. At the root of the vanes the impeller disk and the casing channel approach closely, preventing substantial flow out of the channel and across the disk. In the turbine pump the liquid may pass over several blades, acquiring an increment of momentum with each passage before reaching the discharge port, and the number of impulses received from the blades depends on the discharge pressure and the speed of rotation. After the liquid makes nearly a complete revolution in the casing channel, it is diverted to the discharge. Pressure in the channel is a minimum at the suction opening and gradually increases to the discharge port. In contrast with a centrifugal pump where the suction flow should

be directed axially into the eye of the impeller, the flow into a turbine pump may be directed to the periphery of the wheel.

The pumping characteristic for a turbine pump is intermediate between the constant-volume characteristic of a positive displacement pump and the constant-head characteristic of a centrifugal pump. The power consumption of turbine pumps increases with increasing discharge pressure and decreasing flow, approaching maximum at zero flow. As a result, overheating of the pump and contents may occur unless provision is made to circulate sufficient liquid for cooling purposes when very high heads or low flows are encountered. Where properly applied, turbine pumps are equal in efficiency to centrifugal pumps, especially for higher heads per stage at flow rates below 200 gal./min.

**Propeller pumps** use an open impeller which resembles the screw or propeller of a ship, so that the surfaces of the moving blades thrust and lift the liquid, imparting increased velocity in forward and tangential directions. Stationary guide vanes convert the tangential, rotary velocity into a forward velocity, thus increasing the useful velocity head of the stream. A divergent passage at the outlet converts velocity head

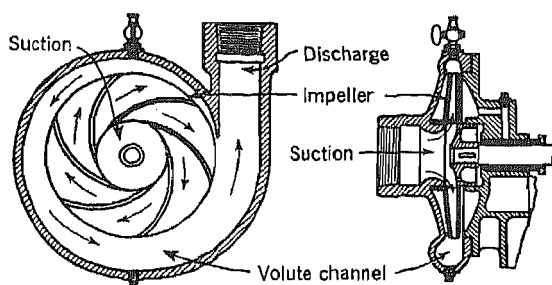


Fig. 3. Volute centrifugal pump.

into pressure head. Propeller pumps are largely used for pumping very large volumes of liquid against low-resisting heads.

**Centrifugal Pumps.** Higher pumping heads than those achieved by the propeller pump may be obtained by designing the impeller vanes to direct the flow radially outward from the impeller axis so that the head of fluid is increased by centrifugal force. As the component of radial flow is increased with respect to the component of axial flow, a continuous series of impeller designs is possible, ranging from wholly axial flow through mixed axial and radial flow to wholly radial flow. Commercial centrifugal pumps thus cover a wide range of impeller designs from the mixed flow to the true radial flow characteristics and are loosely classified as *mixed flow*, *volute type*, and *diffuser type*, of which the last two are strictly centrifugal pumps in which the pressure is principally developed by the action of centrifugal force. A centrifugal pump in its simplest form is an impeller rotating in a volute casing (Fig. 3). Although the pump impeller is the only moving part, the design of the pump inlet and the discharge flow passages are of equal importance because of the high liquid velocities involved.

Because of simplicity, low cost, and adaptability to a wide range of conditions, centrifugal pumps are the most widely used types. Except for the strength of the pump casings, there is virtually no upper limit to the capacity or head for which a centrifugal pump may be designed. Multiple stages in a single casing may be used for higher heads, and liquids of any viscosity which will flow into the pump may be

handled. In recent years, centrifugal compressors for gases have been greatly improved and are likely to replace reciprocating compressors as the preferred high-pressure pump for gases where large volumes are handled at inlet densities greater than atmospheric air.

Centrifugal pumps sometimes lose discharge head or fail to build up head due to the presence of gas or vapor in a liquid pump. This is called "loss of prime." Gas or vapor in the suction line tends to become separated from the liquid and to accumulate in the eye of the impeller, thus preventing liquid from entering the pump. For this reason, the suction piping to a centrifugal pump should be arranged to avoid the accumulation of vapor in pockets which may be swept into the pump by a surge of liquid, as when starting the pump flow. Cavitation occurs when the pressure head is reduced at any location in the pump to a value below the vapor pressure of the liquid. Formation and collapse of bubbles inside the pump as the fluid flows through a region of low pressure results in noise, vibration, unbalance, and shortened life of the pump. Hence, care must be taken to design the suction piping so that the pressure head at the pump inlet can never fall to a value less than the sum of the vapor pressure of the liquid and the net positive suction head stated by the pump manufacturer. In general, the maximum efficiency that can be achieved in centrifugal pumps decreases with the capacity. The greater loss in small centrifugal pumps is due to the larger amount of wetted surface per volume of liquid pumped, which causes dissipation of relatively more energy through friction and turbulence.

#### PUMP SELECTION

The problem of pump selection usually should not be attempted by the chemical engineer but should be delegated to the pump specialist, who is more competent to coordinate the requirements of the pump and drive; of the hydraulic and driving controls; and of the bearings, gaskets, and stuffing boxes. Certain general considerations, however, must be resolved by the chemical engineer before presenting the problem to the pump specialist. Foremost among these are the process and economic requirements, including problems of corrosion, leakage, and contamination, as well as the economical arrangement of the pumping system as a whole.

Since the pump itself may be but a minor element of cost and yet may have a profound effect on the cost of the whole system, the economic evaluation of the pump is more complex than a balance between capital cost and energy expense. In addition to maintenance expense, the cost of leakage and especially the cost of lost production caused by pump failure must be considered. In chemical plants the cost of down-time is usually so important a factor that reliability in a pumping system is dominant over initial cost and mechanical efficiency.

The process considerations for a specified service usually influence pump selection by eliminating from consideration those types of pumps which cannot meet the process requirements for pressure, temperature, capacity, suction pressure, speed, and materials of construction. For flows below a few gallons per minute, positive displacement pumps are appropriate. For flows greater than 200 gal./min., centrifugal pumps are suitable. The choice of pump type in the range between 5-200 gal./min. depends on the head, capacity, and power characteristics which are most appropriate for the service. Positive displacement pumps are particularly useful to provide fairly constant flows against a variable discharge head, while centrifugal pumps are particularly useful to provide a fairly constant pressure throughout a variable flow range. The

turbine pump provides a characteristic which is intermediate between the positive displacement type and the centrifugal type.

For applications where flow metering and control by means of auxiliary instruments are not feasible, it is possible to secure reciprocating pumps which have been especially designed to minimize slip. These pumps may be employed for metering a liquid at a constant rate depending upon the speed and displacement of the pump, either of which may be adjustable by hand or automatic controls, if desired. Such metering pumps are also available in corrosion-resistant materials if required, such as a diaphragm-type pump with a porcelain body.

### MATERIALS OF CONSTRUCTION

Materials of construction for fluid transportation are commercially available in expanding variety to meet a wide range of special requirements for corrosion, abrasion, and contamination. Pipe, valves, fittings, and pumps can be supplied in nearly all of the commercial metals and alloys. In addition, an increasing number of nonmetallic materials are in commercial supply, particularly among the plastics. Table I indicates the equipment forms in which many of these nonmetallic materials are supplied by two or more fabricators.

TABLE I. Nonmetallic Materials of Construction.

Material	Commercially available in		
	Pipe and fittings	Valves	Pumps
Ceramics:			
Glass.....	+	+	+
Porcelain.....	+	+	+
Fused silica.....	+	—	—
Stoneware.....	+	+	+
Carbon and graphite.....	+	+	+
Plastics:			
Furan-asbestos or graphite.....	+	+	+
Nylon.....	+	—	—
Phenolic-asbestos or graphite.....	+	+	+
Polyethylene.....	+	—	—
Polyvinyl chloride.....	+	+	+
Saran.....	+	—	—
Styrene.....	+	—	—
Vinylidene chloride.....	+	—	—
Rubber:			
Natural, compounded.....	+	+	+
GR-S.....	+	+	+
GR-A.....	+	+	+
Neoprene.....	+	+	+

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**FLUOALUMINATES.** See "Aluminum compounds" under *Fluorine compounds, inorganic*.

**FLUOBERYLLATES.** See *Beryllium*, Vol. 2, pp. 494-95, 498; "Beryllium fluoride" under *Fluorine compounds, inorganic*.

**FLUOBORATES; FLUOBORIC ACID,  $\text{HBF}_4$ .** See "Boron compounds" under *Fluorine compounds, inorganic*.

**FLUOPHOSPHATES; FLUOPHOSPHORIC ACIDS.** See "Phosphorus compounds" under *Fluorine compounds, inorganic*.

**FLUOR-.** See also terms beginning with *Fluo-* and *Fluoro-*.

**FLUORAN DYES.** See *Colors for foods, drugs, and cosmetics*, Vol. 4, pp. 292-93, 297-303; *Xanthene dyes*.

**FLUORANTHENE,  $\text{C}_{16}\text{H}_{10}$ .** See *Hydrocarbons*.

**FLUORAPATITE,  $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ .** See *Fertilizers*; "Hydrogen fluoride" under *Fluorine compounds, inorganic*; *Phosphoric acids and phosphates*.

**FLUORENE,  $\text{C}_{13}\text{H}_{10}$ ; 9-FLUORENONE,  $\text{C}_{13}\text{H}_8\text{O}$ .** See *Hydrocarbons*; *Ketones*.

**FLUORESC EIN,  $\text{C}_{20}\text{H}_{12}\text{O}_5$ .** See "D&C Yellow No. 7" under *Colors for foods, drugs, and cosmetics*, Vol. 4, p. 301; *Indicators*; *Xanthene dyes*.

**FLUORESCENT LAMPS.** See *Lamp manufacture*.

**FLUORESCENT MATERIALS.** See *Luminescent materials*.

**FLUORIDES.** See *Fluorine compounds, inorganic*.

**FLUORIMETRY.** See *Colorimetry and fluorimetry*.

**FLUORINATION.** See *Fluorine compounds, organic*.

## FLUORINE

Fluorine, F, atomic number 9, atomic weight 19.00, is a nonmetallic element, which exists as a very pale yellowish gas,  $\text{F}_2$ , with an intense, highly irritating odor somewhat resembling chlorine and ozone. The name is derived indirectly, through fluorspar, from the Latin *fluere*, meaning to flow, in allusion to the well-known fluxing power of that mineral. Only one stable isotope,  $\text{F}^{19}$ , is known, although the radioactive isotopes  $\text{F}^{17}$ ,  $\text{F}^{18}$ , and  $\text{F}^{20}$  have been reported. Fluorine, the first member of Group VII of the periodic table, has the electronic configuration: 2, 1s; 2, 2s; 5, 2p. It has a valence of -1. It is similar to the other halogens in many respects but, as is usually the case with the lightest member of a family of elements, it exhibits some noteworthy differences and a tendency to resemble a neighboring element in the same period (oxygen). Chemically, fluorine is the most reactive nonmetal. It does not occur free in nature, but, in combination, is about as abundant as carbon or nitrogen on the earth's surface and about as plentiful as chlorine in the lithosphere.

Scheele, in 1771, recognized the volatile product obtained by treating fluorspar (*Flussspat*) with sulfuric acid as a new and distinct mineral acid (*Flusssäure*). Gay-Lussac and Thénard prepared a pure concentrated solution of hydrogen fluoride in 1809, but believed the acid to be an oxy compound of the new element they called *fluorium*. Frémy, in 1856, was the first to prepare anhydrous hydrogen fluoride. In 1812, Ampère suggested that the acid contained no oxygen, proposed the name *fluor* for its nonmetallic constituent, and suggested its liberation by electrolytic means.

It was not until 1886, however, after more than 75 years of research by many experimenters, that the element was finally isolated. Moissan first produced fluorine by electrolyzing a solution of potassium bifluoride in anhydrous hydrogen fluoride at  $-23^{\circ}\text{C}$ . in a platinum U-tube, between platinum-iridium electrodes. In the years intervening between its discovery and the awakening of a general interest in fluorine in the early 1920's, the major contributions to our knowledge of fluorine chemistry were made by Ruff and his students in Germany (36).

At the present time, fluorine is used principally for the production of inorganic and organic fluorine compounds which cannot be made by other methods. For example, the manufacture of fluorine was greatly accelerated during World War II because of the use of the element in preparing uranium hexafluoride for isotope separation in the atomic energy project.

See also *Fluorine compounds, inorganic*; *Fluorine compounds, organic*.

### Physical and Chemical Properties

#### CONSTANTS

Fluorine can exist as a very pale yellowish gas, as a canary-yellow liquid, or as a light yellow solid, which becomes colorless below  $-252^{\circ}\text{C}$ . Its physical properties have been reported as follows (5,12): m.p.,  $-217.8^{\circ}\text{C}$ .; b.p.,  $-188^{\circ}\text{C}$ .; weight/vol. at  $-223^{\circ}\text{C}$ . (solid), 1.3 grams/ml. (approx.), at b.p. (liquid), 1.108 grams/ml., at S.T.P. (gas), 1.695 grams/liter; vapor pressure,  $\log p_{\text{mm.}} = 9.175 - 442.72/T - 0.013150T$ ; surface tension at  $-216^{\circ}\text{C}$ ., 14.61 dynes/cm., at  $-188.2^{\circ}\text{C}$ ., 9.85 dynes/cm.; heat capacity, 6.80 cal./(gram-mole)( $^{\circ}\text{C}$ .); heat of fusion, 390 cal./gram-mole (approx.); heat of vaporization, 1540-1580 cal./gram-mole; crit. temp.,  $-129^{\circ}\text{C}$ .; crit. pressure, 55 atm.; dielectric constant at  $-183.6^{\circ}\text{C}$ ., 1.556, at  $-185.5^{\circ}\text{C}$ ., 1.487.

#### REACTIONS

Fluorine is the most reactive nonmetal, having a higher oxidation potential than ozone. It is the most electronegative of the elements, the normal fluorine electrode potential being 2.85 volts as compared with 1.36 volts for chlorine and 1.22 volts for oxygen, the next most active nonmetals. It combines, directly or indirectly, to form the fluorides of all other elements except the Group 0 gases. Fluorine reacts vigorously with most oxidizable substances at room temperature, frequently with immediate ignition. Some of the resulting fluorine compounds, such as chlorine trifluoride, are exceptionally reactive chemically; others are more stable than the analogous chlorine compounds; and still others, such as sulfur hexafluoride, nitrogen trifluoride, the Freon compounds, Kel-F (polymerized chlorotrifluoroethylene), Teflon (polymerized tetrafluoroethylene), and the fluorocarbons, are outstandingly inert.

**Other Elements.** Solid fluorine and liquid hydrogen combine with explosive violence to form hydrogen fluoride, HF. Reaction between the two gases is also generally very energetic. There have been reports, however, that this reaction proceeds at relatively slow rates under certain conditions; the difference may be due to the material of which the containing vessel is made. The reaction appears to be a chain mechanism with a marked induction period and to have a high activation energy as well as a high reaction energy. The other halogens combine with fluorine to form halogen fluorides of the type ClF, ClF<sub>3</sub>, BrF<sub>3</sub>, IF<sub>5</sub> (10). Oxygen does not react directly with fluorine under ordinary conditions, although two oxygen fluorides, OF<sub>2</sub> and O<sub>2</sub>F<sub>2</sub>, are known.



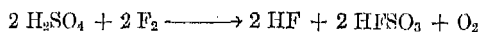
Amorphous forms of carbon react with fluorine in the cold to form a mixture of fluorides in which  $\text{CF}_4$  and  $\text{C}_2\text{F}_4$  or  $\text{C}_2\text{F}_6$  predominate; graphite must be heated to redness to initiate reaction (23,40). Nitrogen does not react with fluorine and may be used as a diluent for the latter in vapor-phase reactions (23). Nitrogen trifluoride,  $\text{NF}_3$ , is best made indirectly by the electrolysis of molten ammonium bifluoride,  $\text{NH}_4\text{HF}_2$ . The other nonmetals form normal fluorides, for example,  $\text{BF}_3$ ,  $\text{SiF}_4$ , and  $\text{SF}_6$ .

Most of the metals are attacked by fluorine at ordinary temperatures, but many of them form protective fluoride coatings which effectively prevent further reaction. Thus, lead reacts vigorously in the cold; aluminum, iron, chromium, and nickel are examples of metals which form protective films in the cold but which will react with incandescence if heated; mercury forms a protective surface coating which inhibits further reaction provided the surface remains undisturbed; copper and gold are attacked appreciably only at high temperatures. The metal fluorides generally melt at lower temperatures than the other halides; the higher fluorides of the heavy metals are frequently gases or volatile liquids.

**Oxides and Hydroxides.** Fluorine dissolves in and reacts with water to form hydrofluoric acid,  $\text{HF}$ , oxygen fluoride,  $\text{OF}_2$ , hydrogen peroxide, and oxygen (11). Ozone has also been reported as a reaction product. Nitric oxide,  $\text{NO}$ , combines with excess fluorine at  $-80^\circ\text{C}$ . to form nitrogen dioxyfluoride,  $\text{NO}_2\text{F}$ , and nitrogen; excess nitrogen dioxide and fluorine also yield nitrogen dioxyfluoride, whereas excess nitric oxide and fluorine yield nitrosyl fluoride,  $\text{NOF}$ . Neither carbon monoxide nor carbon dioxide reacts with fluorine in the cold (23). Phosphorus pentoxide is converted to a mixture of phosphorus fluorides and phosphoryl fluoride,  $\text{POF}_3$ . Silica is not attacked in the cold in the absence of moisture. Many metal oxides, including sodium, potassium, and calcium oxides, fail to react with fluorine. In contrast, however, solid sodium, potassium, and calcium hydroxides react in the cold to form the metal fluoride, water, oxygen, and oxygen fluoride; in solutions, a peroxide is formed in addition to the compounds just named (11). Lead hydroxide is converted to the dioxide,  $\text{PbO}_2$  (24).

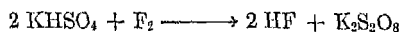
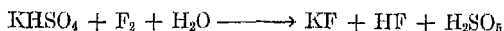
**Halogen Compounds.** Fluorine readily displaces the other halogens from many of their compounds, such as hydrogen chloride and solid metal halides. The reaction with phosgene (carbonyl chloride),  $\text{COCl}_2$ , to form carbonyl fluoride,  $\text{COF}_2$ , proceeds to a limited extent. Carbon tetrachloride is attacked very slightly at ordinary temperatures and has been suggested as a solvent-diluent for fluorine. However, explosions are known to have occurred when concentrations of fluorine have been built up in carbon tetrachloride.

**Acids.** Nitric acid reacts with fluorine to form the explosive gas "fluorine nitrate,"  $\text{NO}_3\text{F}$ . Sulfuric acid when treated with fluorine yields fluosulfonic acid:

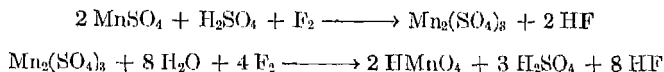


boric acid,  $\text{H}_3\text{BO}_3$ , yields boron trifluoride,  $\text{BF}_3$ ; and phosphoric acid, a mixture of peroxydiphosphoric acid,  $\text{H}_4\text{P}_2\text{O}_8$ , and peroxymonophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_6$  (24).

**Salts.** Potassium bisulfate,  $\text{KHSO}_4$ , in dilute solution reacts with fluorine to yield peroxymonosulfuric acid (Caro's acid),  $\text{H}_2\text{SO}_5$ , and in concentrated solution, potassium peroxydisulfate,  $\text{K}_2\text{S}_2\text{O}_8$ :



Similarly, potassium bicarbonate,  $\text{KHCO}_3$ , yields potassium peroxydicarbonate,  $\text{K}_2\text{C}_2\text{O}_6$ ; sodium phosphate, sodium peroxyphosphate,  $\text{Na}_2\text{P}_2\text{O}_7$ ; and sodium metaborate,  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ , in the presence of excess carbonate, sodium "perborate,"  $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$  (24). Cobaltous salts are oxidized to cobaltic salts. The manganous to manganic conversion is followed by further oxidation to permanganic acid:



Chromic sulfate,  $\text{Cr}_2(\text{SO}_4)_3$ , is converted to chromium trioxide,  $\text{CrO}_3$ , and thence to peroxy chromic acid, which then reacts with the hydrogen fluoride formed by the reaction to yield chromic fluoride,  $\text{CrF}_3$ , and oxygen. Silicates react readily with fluorine; it is possible to maintain the continued combustion of glass and asbestos in fluorine.

**Organic Compounds.** The reaction of organic compounds with fluorine is generally very violent (ignition or explosion) with total disintegration of the molecule; hydrogen fluoride, carbon fluorides, and carbon are the usual products. Under controlled conditions, however, for example when diluted with nitrogen gas or when brought together in restricted volumes, hydrocarbon vapors may be fluorinated with elemental fluorine in the presence of a heat-conducting packing. Hydrocarbon vapors are also fluorinated in the presence of a catalyst or fluorine carrier such as the polyfluorides of cobalt or silver.

### Occurrence

Fluorine does not occur free in nature except, perhaps, in trace amounts as occlusions in certain fluorspar occurrences associated with radioactive minerals. Recent estimates indicate that fluorine constitutes approximately 0.08% of the lithosphere and 0.001% of the hydrosphere, and, as such, ranks about thirteenth among the elements in order of abundance. Fluorspar (fluorite),  $\text{CaF}_2$ , is the most important source of fluorine and its compounds; cryolite,  $\text{Na}_3\text{AlF}_6$ , ranks second in importance among the fluorine minerals. Appreciable quantities of fluorine are present in fluorapatite,  $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ , and other phosphate rocks. The minerals fluellite,  $\text{AlF}_3 \cdot \text{H}_2\text{O}$ , and topaz,  $(\text{AlF}_2)_2\text{SO}_4$ , contain fluorine as a major component; tourmaline and some species of hornblende and mica also contain smaller amounts of fluorine.

In animal organisms, fluorine concentrates in the calcareous parts of the anatomy (bones, teeth, marine shells, etc.). The physiological action of fluorine, particularly as it affects dental caries and mottling of the enamel, is of increasing interest in the field of water treatment and has been studied in detail (27). See also *Water, industrial and municipal*.

### Manufacture

The principle of rendering liquid anhydrous hydrogen fluoride electrically conducting by dissolving in it a metallic fluoride remains the basis of all present-day methods of fluorine manufacture. As shown in Table I, modern fluorine cells have developed through a gradual modification of Moissan's first cell. Of these, the Harshaw Chemical Company's 1000-ampere cell, Du Pont's 1500-ampere cell (16), the Hooker Electrochemical Company's 2000-ampere cell, and the Pennsylvania Salt Manufacturing

TABLE I. Characteristics of Important Fluorine Cells.

Name	Year	Electrolyte	Temperature, °C.	Vessel	Electrodes		Current, amp.	Volts	Current efficiency, %	Diaphragm	Anode insulation	Cell type	Ref.
					Anode	Cathode							
Moissan	1886	KHF <sub>2</sub> in HF	-15	Pt-Ir	Pt or Pt-Ir	Pt or Pt-Ir	3.5-4.5	50	30	—	Fluorspar	U-tube	(31)
Ruff	1899	KF in HF	-15	Copper	Platinum	Platinum	2-7	40-66	30	—	—	—	(37)
Poulenc	1900	HF	-15	Copper	Platinum	Copper	—	—	—	Copper	—	—	(35)
Gallo	1910	HF	-15	Platinum	Platinum	Platinum	—	—	Very low	—	—	—	(21)
Argo	1919	KF, HF	225-250	Cu, later graphite	Graphite	Copper	10	12-15	70	Copper	Fluorspar	Pot	(6)
Ruff	1920	KF, 1.8 HF	240	Copper	Graphite	Copper	9-10	14-16	—	—	—	—	(36)
Meyer	1920	KF, HF	240-250	Graphite	Graphite	Graphite	10-15	10	68-75	—	—	—	(28)
Simous	1924	KF, HF	200-220	Copper	Graphite	Copper	10-15	10-20	70	Copper	Portland cement	Pot	(39)
Lebeau	1925	KF, 3 HF	55	Copper	Nickel	Copper	—	—	Very good	Copper connected to anode	—	—	(26)
Baneroff	1929	KF, HF	220-300	Magnesium	Graphite	Magnesium	5-6	—	30	Magnesium	Portland cement	Pot	(7)
Fredenhagen	1929	KF, 1.6 HF	160-250	Copper	Graphite	Copper	30	10	92-98	—	—	—	(19)
Jones	1929	KF, HF	220-300	Magnesium	Graphite	Magnesium	5-6	—	30	Magnesium	Portland cement	Pot	(24)
v. Wartenberg	1930-40	KF, 3 HF	70	Copper	Nickel	Copper	6	—	76	—	—	—	—
Dennis	1931	KF, HF	230-280	Copper	Graphite	Graphite	5-10	12-18	75	—	Bakelite cement	V-tube	(15)
Du Pont	1932	KF in HF	50	Nickel	Pt, Ni, Cu	Ni, Fe, Cu, Mg	—	—	—	—	—	—	(43)
Denbigh	1934	KF, HF	220	Copper	Graphite	Copper	15	—	80	Copper	—	—	(14)
Bodenstein	1935	KF, HF	250	Elektron	Graphite	Silver	—	—	75-80	—	—	—	(9)
Miller	1935	KF, HF	250	Nickel	Graphite	Graphite	5	18-20	61-89	—	Cement of fluorspar and sodium silicate	U-tube	(30)



Company's 2000-ampere cell may be considered units of commercial size. See also reference (2).

In the U.S., the Pennsylvania Salt Manufacturing Company began the manufacture and marketing of fluorine in 1946. Before this, major quantities of fluorine had been produced only for the atomic energy project.

**Pennsalt 250-Amp. Cell.** For small-scale work, the simple and reliable fluorine generator shown in Figure 1 has proved satisfactory. This cell consumes 250 amp. at 8.5-9.0 volts and produces about  $\frac{1}{8}$  lb. of fluorine per hour (20). The electrolyte, potassium bifluoride,  $\text{KHF}_2$ , plus hydrogen fluoride, analyzing 38-40% HF, is maintained at 105-110°C. The anodes are type GA carbon plates and the cathodes are louvered steel sheets, which direct the flow of liquid and hydrogen gas bubbles upward and away from the anode. No diaphragm is needed in this type of cell; the barrier in the space above the electrolyte effectively prevents the recombination of the hydrogen and fluorine. German fluorine cells were generally similar to the unit just described; cells developed in the U.S., however, have usually been equipped with a diaphragm to separate the anode and cathode spaces.

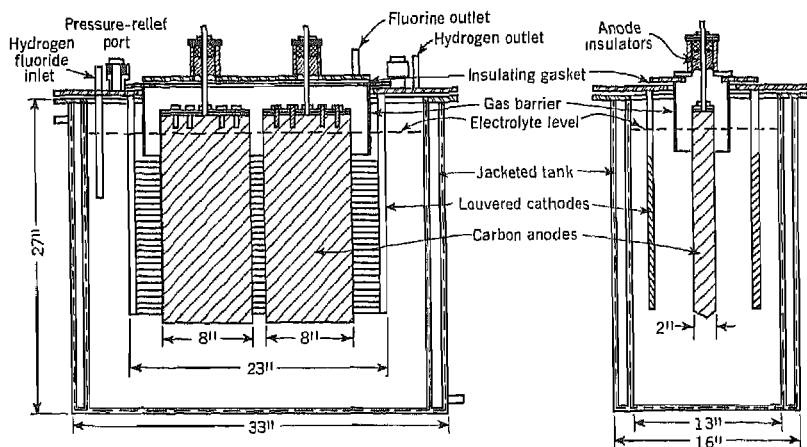


Fig. 1. Pennsalt 250-amp. fluorine cell (20).

**Pennsalt 2000-Amp. Cell.** Two of these commercial cells are shown in Figure 2. They are structurally similar to the 250-amp. laboratory-scale model just described. The materials of construction, electrolyte composition, and the method of operation are identical. The large cell, however, employs sixteen 2 in.  $\times$  5 in.  $\times$  24 in. carbon anodes as compared with two 2 in.  $\times$  8 in.  $\times$  18 in. anodes in the laboratory model.

In Figure 2, a spare anode cover, showing the bus bar and its supports and the anode connectors, appears at the left. The view of the cells shows explosion ducts running the length of the cell and, at the far end, the connecting ducts between the explosion ducts and the disposal scrubbing tower. The cone-topped cylindrical chamber at the rear is the fluorine disposal unit in which fluorine to be discarded is burned with illuminating gas. At the near end of the cells are seen the two hydrogen outlets (light-gray inverted U's) with their rubber-hose current breaks. Directly in front of the rubber sections is the hydrogen fluoride make-up line with its valved branches to either side of the cell. Still lower is the fluorine exit line with its flanged connection to the cell and electrolyte catchpot (the short vertical section of 4-in. pipe).

**Harshaw 1000-Amp. Cell.\*** This cell was developed to operate continuously over extended periods of time with little attention. It uses ordinary carbon steel for the major parts of the cell, including the cell body, the hot-water jacket, the hydrofluoric acid feed line, the cathode, and the solid part of the diaphragm that extends from the head of the cell down into the electrolyte for a depth of about 2 in. The cathode is about  $\frac{1}{4}$  in. thick and perforated, to permit easy circulation of the electrolyte. The porous part of the diaphragm is a Monel screen, silver-soldered into a slot in the lower

\* Information from Harshaw Chemical Company.

edge of the solid part of the diaphragm. This has eliminated most corrosion problems. The anodes are made of copper-impregnated carbon rods. They are 12 in. long and 1.25 in. in diameter. The electrolyte is fused  $\text{KF} \cdot 2\text{HF}$  with 1–1.5% lithium fluoride as additive. Figure 3 shows a simplified drawing of this cell. It holds 1675 lb. of electrolyte which fills the cell to a depth of 19 in.

The cell operates at 95–115°C. with an anode current efficiency close to 95% and an overall potential drop of 9.0–9.5 volts. Such large cells have operated continuously with very little attention for more than 13 months. More details on this cell will be found in reference (34).

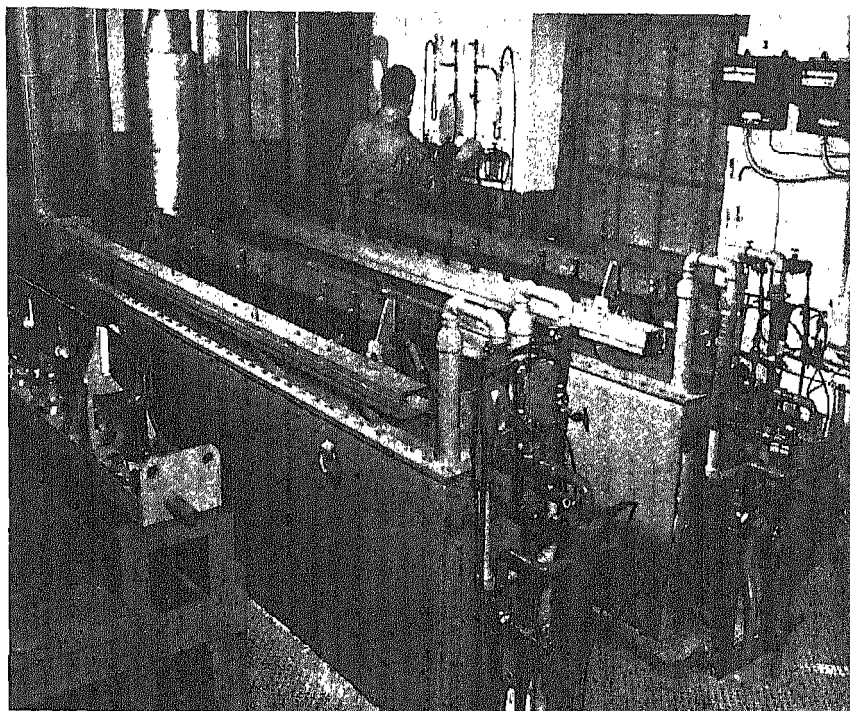


Fig. 2. Pennsalt 2000-amp. fluorine cell.

**Hooker 2000-Amp. Cell.\*** The design and development of this cell were started in 1942 at the request of the Office of Scientific Research and Development of the U.S. Government. The cell design was based on two premises. First, that the current density at the electrodes should be kept as low as possible to avoid polarization. This is particularly necessary in carbon anode cells. To achieve this, as many parallel electrodes as possible should be packed into the smallest possible space. Secondly, to reduce the time consumed in replacements under plant-operating conditions, the cell construction should be as simple as possible. The order of probable failure is anodes, diaphragms, and cathodes. These components are therefore built in assemblies, which are removed in the order mentioned. Shortening the shut-down time for renewals of parts can be greatly facilitated by having spare assemblies already prepared rather than installing individual small parts in the cell.

The cell consists of four main parts (see Fig. 4): (1) A steam-jacketed steel tank contains the electrolyte. This tank is fitted with a steel cover into which are welded long, parallel, boxlike inserts open at top and bottom, and in number depending upon the size of the cell. (2) The steel cathode assemblies are suspended by three insulators through the cover. (3) The screen diaphragm assemblies are lowered from above into the boxlike inserts, being supported by ledges at the bottom. (4) The anode assemblies consist of two parallel rows of seven carbon blades, 18 in.  $\times$  6½ in.  $\times$  1½ in., each fastened by four bolts and a copper cover plate to a heavy inverted copper channel. The anode assemblies are suspended by two insulators from flat plates that form the tops of the boxlike inserts.

\* This section by S. G. Osborne.

The contact surfaces between carbon anode and copper are made with a carbon-water paste, which is baked dry.

Following this plan all parts can then be removed in the order: anode, diaphragm, cathode.

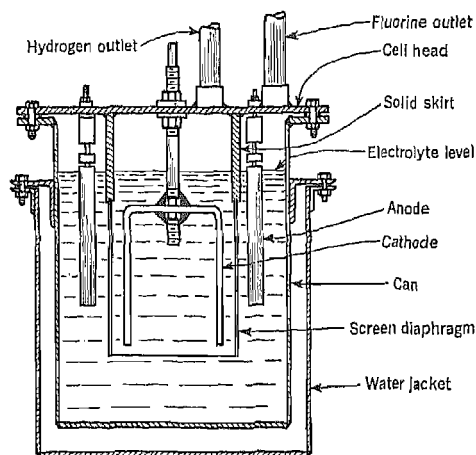


Fig. 3. Harshaw 1000-amp. fluorine cell (34).

amounts of carbon dioxide, oxygen, nitrogen, and other inerts may also be present. Cell operating temperature is an important factor in controlling the amount of hydrogen fluoride present in the product. The hydrogen fluoride content may be reduced to about 0.5% by a combination of refrigeration and absorption by solid porous sodium fluoride.

### Handling

The safe handling of fluorine has been studied in detail (20,25,29,41). All equipment that comes in contact with fluorine must be completely dry. Metal filings, oxide scale, and dirt should be carefully removed from all pipes and fittings. It is most essential that all traces of paint, oil, grease, and other organic materials be eliminated, otherwise the temperatures generated by the reaction of such impurities with fluorine may be sufficiently high to ignite the metal parts. At atmospheric pressure, the gas can be conducted in standard or extra-heavy steel pipe or in copper tubing of adequate weight. However, both steel and copper develop a protective film, which may be dislodged by flexure or vibration and, by accumulating in restricted parts, cause line stoppages. Where the formation of fluoride scale must be avoided, and in high-pressure work, the use of Monel or nickel-alloy piping is recommended. Taper-threaded pipe connections are satisfactory for fluorine at low

Only one hydrogen outlet and one fluorine outlet are required for each cell with one set of electrodes for 1000 amp., two sets of electrodes for 2000 amp., and more for larger cells. Both sides of the anode blades are utilized, the lower 12 in. being active. At full load the cell operates at  $7\frac{1}{2}$  amp. per square foot,  $8\frac{1}{2}$ -9 volts, and 90-95% current efficiency. The electrolyte is essentially  $\text{KF} \cdot 2\text{HF}$ , and the operating temperature is in the range 95-105°C. Anhydrous hydrogen fluoride gas is fed to the cell as make-up and a little nitrogen is introduced through the same tube to prevent suckback of electrolyte. The anodes have a life of several months; diaphragms have lasted two years and more; and cathodes and cell bodies have been in operation over six years, appearing to be almost indestructible.

Hydrogen fluoride is the principal impurity in fluorine and may be present to the extent of 5% or more by weight. Small

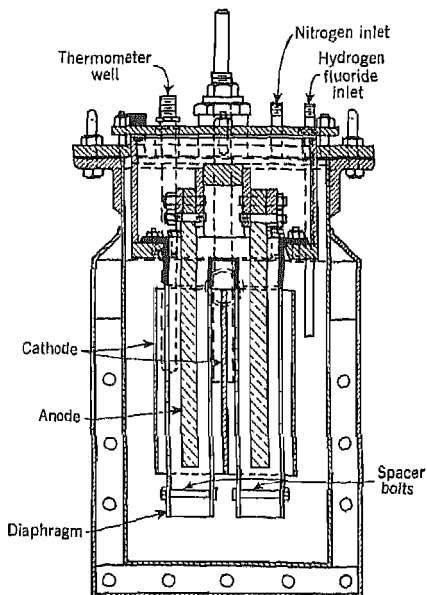


Fig. 4. Hooker 2000-amp. fluorine cell (32).

pressure and temperature. The recommended lubricant for pipe threads is a water-base graphite paste or a composition of calcium fluoride in a completely fluorinated oil; this lubricant should be applied only to the external thread with none on the parts that will be subsequently exposed to fluorine. Flanged joints, with Teflon gaskets for low-pressure work and soft copper or aluminum gaskets for high pressures, are also recommended. Globe or needle-type valves with Monel or nickel stems and seats and Teflon packing are suitable. Diaphragm, bellows, and other types of packless valves are satisfactory if the operating mechanism in contact with the fluorine is not readily made inoperative by fluoride scale. Gages should employ steel Bourdon tubes. After use all equipment should be flushed clean of fluorine with an inert gas such as dry nitrogen, and all outlets should be closed immediately to prevent the influx of atmospheric moisture.

Fluorine is shipped in steel cylinders, with specially packed valves, under a pressure of 400 p.s.i. These cylinders conform with I.C.C. specification 3A2000 and bear a red label. The major part of the fluorine required by industry, however, is being generated at the point of utilization.

### Analysis

In the analysis of fluorine gas, hydrogen fluoride is first removed by absorption in solid sodium fluoride, sodium bifluoride being formed quantitatively (41). The fluorine is then "converted" to chlorine by passage through anhydrous sodium chloride, and the resulting gas mixture is analyzed for chlorine, oxygen, and inert gases by standard methods.

### Health and Safety Factors

The hazard of exposure to fluorine in the atmosphere is at least as great as for chlorine. Fluorine will cause deep penetrating burns on contact with the body, and the effect may be delayed and progressive with ensuing necrosis and ulceration, as in the case of burns by hydrogen fluoride (25,29,42). Protective measures against fluorine have not yet been fully developed, and entry into zones contaminated with fluorine should be avoided. Only air-line or oxygen masks can be recommended at the present time for personal protection against fluorine-containing atmospheres. Neoprene gloves and face shields can give only temporary protection against fluorine; if they are brought in local contact with fluorine at high concentration, they will inflame. A fabric consisting of fireproof neoprene on a Fiberglas base has been found most resistant to blasts of fluorine (25). Therefore, safety clothing can give very little protection against fluorine. For working with elemental fluorine at elevated pressure, the apparatus that is to contain the fluorine should be surrounded by a protective barrier of steel at least  $\frac{1}{4}$  in. thick, and all valves should be operated by remote control. Such rigorous precautions are not necessary with fluorine when used at low pressures.

### Present Uses and Future Prospects

Before World War II, fluorine was generated in very small quantities for experimental purposes, and could not be purchased at any price. Technological developments during the war have made it possible to produce it on a large scale at reasonable cost. Elemental fluorine is now used in commercial quantities for the production of



such compounds as uranium hexafluoride, which was used in the separation and concentration of uranium isotopes in connection with the atomic bomb project; sulfur hexafluoride, which is used as an insulating gas in high-voltage equipment because of its high dielectric strength and chemical inertness; chlorine trifluoride, which is nearly as active chemically as fluorine itself, but which, unlike fluorine, can be shipped in liquid form in cylinders; and the metal polyfluorides ( $\text{AgF}_2$ ,  $\text{CoF}_3$ ,  $\text{MnF}_3$ ), which are valuable fluorinating agents in the production of fluorocarbons.

On the basis of the abundance and availability of fluorine raw materials and the unique physical and chemical properties of fluorine compounds, it is to be expected that the industrial utilization of fluorine chemicals will continue to increase. See also "Hydrogen fluoride," under *Fluorine compounds, inorganic*.

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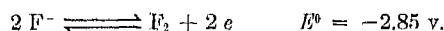
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H. C. MILLER AND F. D. LOOMIS

## FLUORINE COMPOUNDS, INORGANIC

Most inorganic fluorine compounds are included in this article. The fluorides of a few elements, however, are dealt with in the articles on these elements and their compounds; the more important of these fluorides are entered alphabetically in this article with appropriate cross references.

The fluorine atom has the electronic structure  $1s^2, 2s^2, 2p^5$ . It can, therefore, be expected to attain a stable electronic configuration either by gaining one electron to form a fluoride ion or by sharing electrons to form a covalent bond. Theoretically, as an element in the first row of the periodic system, fluorine is limited to a maximum of four covalent bonds; in practice, it apparently never exceeds one, in contrast to the other elements of the halogen family. Fluorine is the most electronegative of the elements; consequently, the bonds formed by it will usually have an appreciable degree of ionic character. The stability of the fluoride ion is reflected in the standard electrode potential,  $E^0$ , for the couple:



The chemical activity of elemental fluorine is due not only to the high electron affinity but also to the relatively weak bonding in the fluorine molecule, this being 24.5 kg.-cal./gram-mole less than in chlorine.

The chemistry of fluorine and its compounds differs in many respects from that of the other halogens. It is the only element of the group sufficiently electronegative to form hydrogen bonds. This type of binding accounts for the association of hydrogen fluoride in the liquid and gaseous states and for the existence of the  $\text{HF}_2^-$  ion, in which the two fluoride ions are linked through the hydrogen. These ions are present in aqueous solutions of hydrogen fluoride and occur as structural units in compounds such as potassium bifluoride,  $\text{KHF}_2$ , a type unknown in the chemistry of the other halogens.

Fluorine apparently does not form very stable bonds with oxygen. No oxy anions have been conclusively demonstrated. Moreover, the two known oxygen fluorides,

$\text{OF}_2$  and  $\text{O}_2\text{F}_2$ , decompose into the elements on heating, the former at about  $250^\circ\text{C}$ ., the latter at  $-95^\circ\text{C}$ . A few other fluorine compounds, such as  $\text{K}_3\text{PbF}_7$ ,  $\text{AgF}_2$ ,  $\text{CoF}_3$ ,  $\text{OsF}_8$ , and  $\text{PtF}_4$ , yield the free element on heating to a readily attainable temperature, whereas most fluorides would require extremely high temperatures for decomposition. Nitrogen fluoride,  $\text{NF}_3$ , is nonexplosive and is more stable than the other nitrogen halides, whereas the compound  $\text{NO}_3\text{F}$  is explosive.

A number of elements exist in a higher oxidation state in their fluorides than in their other halides. The compounds  $\text{AsF}_5$ ,  $\text{SeF}_6$ ,  $\text{SF}_6$ ,  $\text{IF}_7$ ,  $\text{OsF}_8$ ,  $\text{VF}_6$ , and  $\text{MoF}_6$  may be cited as examples. Similarly, the complex fluorides occasionally exhibit higher coordination numbers than is usual for the particular coordination center, as in  $\text{SiF}_6^{2-}$ ,  $\text{TaF}_7^{2-}$ , and  $\text{TaF}_8^{3-}$ . Furthermore, fluorine forms a large number of coordination complexes, which are more stable than the corresponding complexes of the other halogens (if, indeed, the latter complexes are known at all); of particular interest are those formed with elements of Groups III, IV, and V, for example,  $\text{BF}_4^-$ ,  $\text{AlF}_6^{3-}$ ,  $\text{GeF}_6^{2-}$ ,  $\text{PO}_3\text{F}_2^-$ ,  $\text{PF}_6^-$ ,  $\text{C}_6\text{OF}_6^{2-}$ ,  $\text{C}_6\text{OF}_6^{3-}$ ,  $\text{C}_6\text{F}_7^{2-}$ , and  $\text{ZrF}_7^{2-}$ . All of these phenomena may be explained, in part, by the small size and low charge of the fluoride ion.

In naming coordination complexes containing fluorine, the prefix "fluo-" has been used more frequently than "fluoro-." However, since fluoro- has been favored almost universally in names of organic compounds, there is a growing preference for fluoro- in all chemical names. This is reflected in fluorophosphoric acids (see p. 711), whereas the prefix fluo- is still usually found in names like fluoaluminates, fluoboric acids, fluosilicic acid, and fluosulfonic acid (see pp. 671, 684, 725, 734).

The metallic fluorides often differ in crystal structures from the other halides of the same metal. The fluorides generally have structures which may be understood by consideration of the formula type, the radius ratio of cation to anion, and the assumption of nondirectional (ionic) bonds leading to three-dimensional complexes. The other halides usually are built up from chains, sheets, or even molecules in which directional (covalent) forces seem to be operative. These differences are not found in the halides of the very electropositive elements, such as the alkali and alkaline earth metals (except beryllium and magnesium), but are clearly illustrated by the halides of many transition and post-transition metals. Mercuric fluoride, for example, has the (ionic) fluorite type of crystal structure, whereas mercuric chloride forms a molecular crystal.

In some instances, the solubilities of the fluorides are exceptional. The insolubility of calcium fluoride and the rare earth fluorides and the solubility of silver and thallium monofluorides may be noted. The soluble metallic fluorides are toxic. There is evidence, however, that minute amounts of fluoride promote the formation of tooth enamel resistant to caries.

C. R. HOUGH

## Aluminum Compounds.

### Aluminum Fluoride.

Aluminum fluoride,  $\text{AlF}_3$ , formula weight 83.97, is a white crystalline solid, which is used principally as an electrolyte component in the electrolytic reduction and refining of aluminum. Pure anhydrous aluminum fluoride is extremely difficult to prepare; the commercial product generally contains oxyfluoride.

*Properties.* Aluminum fluoride crystallizes in the form of white or transparent

hexagonal rhombohedra; sp.gr. 2.882; sp.heat 0.23 at 15–53°C.; heat of formation 331.5 kg.-cal./gram-mole. A melting point of 1040°C. has been reported, but other work indicates that the salt sublimes without melting, the vapor pressures being (5):

Temperature, °C.....	1098	1144	1218	1275	1291
Vapor pressure, mm. Hg. ....	16.4	60.3	254.7	553.9	760.0

Ruff (8) gives 1260°C. as the sublimation temperature. Aluminum fluoride is insoluble in most inorganic and organic solvents. Its solubility in water is 0.559 gram/100 ml. water at 25°C. Its solubility in aqueous hydrofluoric acid at 25°C. (10) is as follows:

Grams/100 grams saturated $\text{AlF}_3$ soln.											
HF.....	0.77	4.96	10.44	21.08	26.30	30.66	34.07	37.81	41.00	51.80	62.73
$\text{AlF}_3$ .....	0.39	2.74	5.37	16.63	19.68	12.52	13.63	17.07	14.03	7.15	3.53

The known hydrates (5) of aluminum fluoride are:  $\text{AlF}_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{AlF}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ ,  $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{AlF}_3 \cdot \text{H}_2\text{O}$ , and  $\text{AlF}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ . Of these, the hemiheptahydrate,  $\text{AlF}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , is the stable compound up to about 100°C. This hydrate may exist in two forms: an insoluble modification, which is obtained by evaporating a solution of alumina in hydrofluoric acid, and a water-soluble modification, which is produced by adding twice the volume of alcohol to a neutral solution of alumina in hydrofluoric acid.

Aluminum fluoride does not react with water, cold acids, or boiling potassium hydroxide solutions. It is attacked slightly by boiling sulfuric acid and is slowly decomposed by fused sodium carbonate. In the presence of steam at elevated temperatures, it is partially converted to alumina and hydrogen fluoride. Aluminum fluoride forms a number of amines ( $\text{AlF}_3 \cdot \text{NH}_3$ ,  $\text{AlF}_3 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{AlF}_3 \cdot \text{NH}_3 \cdot 2\text{H}_2\text{O}$ ), hydrofluorides ( $3\text{AlF}_3 \cdot 2\text{HF} \cdot 5\text{H}_2\text{O}$ ,  $2\text{AlF}_3 \cdot \text{HF} \cdot 5\text{H}_2\text{O}$ ), and double or complex salts (fluoroaluminates) with the fluorides of ammonium, barium, calcium, cesium, cobalt, copper, iron, lithium, magnesium, nickel, potassium, rubidium, sodium, strontium, thallium, and zinc (6). The most important double fluoride is cryolite,  $\text{Na}_3\text{AlF}_6$ , commercial deposits of which are found in Greenland (see "Cryolite," p. 672).

*Manufacture.* The only simple fluoride of aluminum occurring in the natural state (in Stenna-gwyn, Cornwall) is the rare mineral fluellite,  $\text{AlF}_3 \cdot \text{H}_2\text{O}$ . The manufacture of aluminum fluoride is necessary, therefore, to supply commercial requirements. The major producer and consumer of aluminum fluoride in the U.S. is the Aluminum Company of America.

The process developed by the Pennsylvania Salt Manufacturing Company (1) employs batchwise solution of alumina hydrate in 15% hydrofluoric acid, followed by continuous crystallization, filtration, and calcination. The product is a granular powder assaying 90–93%  $\text{AlF}_3$ .

German processes for the manufacture of aluminum fluoride employ solution of alumina hydrate in hydrofluoric acid at an acid concentration varying from 40 to 60%. The crystallization and calcining operations are discontinuous as contrasted to the American developments (2).

Still another process for the production of aluminum fluoride is that of Gitzen and Wagner (12). In this method, alumina trihydrate, heated between 400 and 700°C., is allowed to react with gaseous hydrogen fluoride.

While all of the known commercial processes for the production of aluminum

fluoride have employed a relatively pure aluminum compound such as alumina or alumina trihydrate as a raw material, a great amount of research and development work has been expended on the use of impure materials such as clays (3,9). The principal difficulty with such materials is the large amount of silica present, which necessitates extensive chemical processing for its removal. Also, the impure aluminum raw materials will contain other metallic elements, such as iron and titanium, which must be removed before use of the aluminum fluoride in the aluminum reduction cells. Thus far, high manufacturing costs have precluded the use of clays as a direct raw material.

A process (11) for making aluminum fluoride that employs the precipitation of an ammonium fluoaluminate intermediate has been developed. The solid is recovered by filtration and decomposed by heating to 700°C., leaving a relatively pure aluminum fluoride.

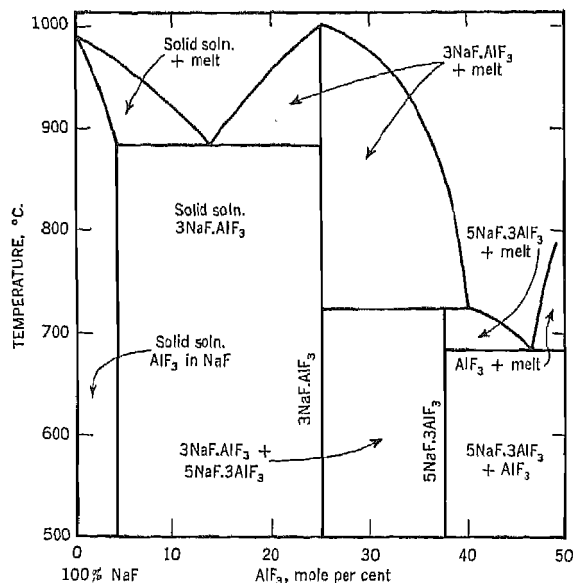


Fig. 1. Phase diagram for the system  $\text{AlF}_3$ - $\text{NaF}$ .

*Specifications and Analysis.* A typical assay of commercial anhydrous aluminum fluoride produced in the U.S. is as follows:  $\text{AlF}_3$ , 82-89%;  $\text{Al}_2\text{O}_3$ , 4-11%;  $\text{Na}_3\text{AlF}_6$ , 1-3%;  $\text{Al}_2(\text{SO}_4)_3$ , 0.2-0.6%;  $\text{SiO}_2$ , 0.2-0.6%;  $\text{Fe}_2\text{O}_3$ , 0.1-0.2%; loss on ignition, 1-4%. The composition of the German product falls within the above range.

The aluminum content of aluminum fluoride may be determined by fusion with potassium bisulfate, followed by solution in water and precipitation as the oxine in ammoniacal solution. The precipitate is filtered and weighed as the oxine after drying. The fluorine content may be determined by fusion with sodium carbonate and solution of the melt in water, followed by the Willard-Winter distillation and titration.

*Uses.* The principal commercial uses of aluminum fluoride are in the electrolytic reduction of alumina in the Hall cell and in the electrolytic refining of aluminum in the Hoopes cell (4). It is employed to vary the fusibility and conductivity of the electrolyte, as shown in Figures 1 and 2, and also the density (7). Aluminum fluoride has

minor applications in the ceramic industry, confined mainly to glass and enamels, in which it serves as a flux for the batch to decrease the viscosity and softening point and to opacify.

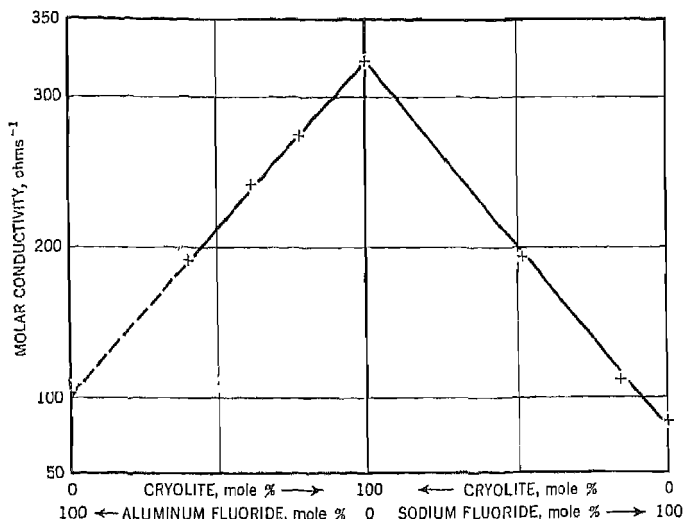


Fig. 2. Effect of aluminum fluoride and sodium fluoride on the conductivity of cryolite melts at 1000°C. (7).

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R. G. DANEHOWER

### Fluoaluminates.

The only important fluoaluminate (fluoroaluminate) is sodium hexafluoroaluminate or cryolite,  $\text{Na}_3\text{AlF}_6$ . Other hexafluoroaluminates such as cryolithionite,  $\text{Na}_3\text{Li}_3(\text{AlF}_6)_2$ , pachnolite and thomsenolite,  $\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}$ , and elpasolite,  $\text{NaK}_2\text{AlF}_6$  (?), occur in nature. Other types of fluoaluminates containing, for example, the anions  $\text{AlF}_4^-$ ,

$\text{AlF}_6^{2-}$ ,  $\text{AlF}_7^{4-}$  (evigtokite,  $\text{Ca}_2\text{AlF}_7 \cdot 2\text{H}_2\text{O}$ ), and  $\text{Al}_3\text{F}_{14}^{5-}$  (chiolite,  $\text{Na}_6\text{Al}_3\text{F}_{14}$ ) are also known.

**Cryolite** (cryolith, Greenland spar, ice-stone) is the mineral form of sodium fluo-aluminate,  $\text{Na}_3\text{AlF}_6$  or  $3\text{NaF} \cdot \text{AlF}_3$ , formula weight 209.97. Natural cryolite, when pure, is colorless to snow-white, transparent to translucent, and has a vitreous to greasy luster; it resembles ice when immersed in water. The first specimens of cryolite were exported from Greenland in 1808, but the mineral did not attain commercial importance until the mid-century. In 1837, the use of cryolite for the manufacture of soda, caustic soda, and alumina was suggested by Tissier, and the process that was developed by Thomsen utilized practically all of the cryolite mined from 1849 to about 1900 (10,16). In the U.S., purified natural cryolite is now marketed under the trade names Kryolith (for use in the metallurgical, ceramic, and abrasive industries), Kryocide (for use as an insecticide), and Rimflux (a special metallurgical grade). Substantial tonnages of synthetic cryolite are also produced for use chiefly in the aluminum industry.

#### PHYSICAL AND CHEMICAL PROPERTIES

*Constants.* Cryolite occurs in the monoclinic form. Upon heating, it undergoes a reversible transition at  $565^\circ\text{C}$ . to an isometric (pseudocubic) modification. Cryolite melts at  $1000^\circ\text{C}$ ., and fusion is accompanied by a substantial volume increase; sp.gr. of solid, 2.95–3.00; of liquid, 2.10 at  $1000^\circ\text{C}$ ., 2.05 at  $1050^\circ\text{C}$ ., and 2.00 at  $1100^\circ\text{C}$ .. The hardness, 2.5 (Mohs' scale) and specific gravity of the solid are said to be increased by fusion. The low refractive index is noteworthy:  $n_D$ ,  $\alpha = 1.3385$ ,  $\beta = 1.3389$ ,  $\gamma = 1.3396$ . The heat of transition at  $565^\circ\text{C}$ . is between 59.0 and 66.7 cal./gram, and the heat of fusion at  $1000^\circ\text{C}$ . is between 73.8 and 79.2 cal./gram. The specific heat of molten cryolite is estimated at 0.38 cal./gram/ $^\circ\text{C}$ .. The true heat capacity of the solid, in cal./gram-mole/degree, at  $T^\circ\text{K}$ ., is:

$$C = 42.133 + 0.042559T - 4.735 \times 10^5/T^2 \quad (\text{below } 565^\circ\text{C}.)$$

$$C = -85.538 + 0.143161T - 165.14 \times 10^5/T^2 \quad (\text{above } 565^\circ\text{C}.)$$

The solubility of cryolite is 0.034 gram/100 grams water at  $15^\circ\text{C}$ ., 0.039 at  $25^\circ\text{C}$ ., and 0.1 at  $100^\circ\text{C}$ .. Cryolite exhibits its greatest solubility in aqueous solutions of aluminum and ferric salts, in which the process of solution is probably accompanied by chemical reaction. Cryolite also exhibits a moderate solubility in solutions of chromium and uranium salts. Sodium fluoride depresses the solubility of cryolite in water.

The solvent action of fused cryolite, particularly for light metal oxides, is an important consideration in the metallurgical applications of this mineral. The electro-

TABLE I. Fusion Temperatures of Cryolite-Containing Mixtures.

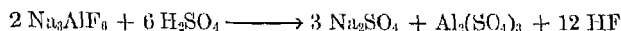
Other component. . . NaF	AlF <sub>3</sub>	CaF <sub>2</sub>	BaF <sub>2</sub>	PbF <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	NaCl	Li <sub>3</sub> AlF <sub>6</sub>
% other com- ponent. . . . . 38.6	39.2	25.4	62.5	40	18	85	62
Fusion temp., °C. 885	685	905	835	730	936	725	730
Other components. NaF + Al <sub>2</sub> O <sub>3</sub>	CaF <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub>	AlF <sub>3</sub> + CaF <sub>2</sub>	AlF <sub>3</sub> + CaF <sub>2</sub> + BaF <sub>2</sub>	NaCl + KCl			
% other com- ponents. . . . . 34 + 12	23.0 + 17.7	37.8 + 6.2	26 + 16 + 18	60 + 25			
Fusion temp., °C. 870	867	675	680	660			

Source: reference (5a).

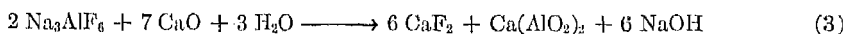
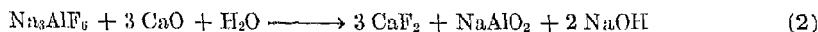
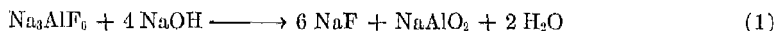
lytic production of aluminum, for example, depends upon the relatively high solubility of alumina in molten cryolite. The oxides of magnesium, calcium, barium, and beryllium are also fairly soluble.

As shown in Table I, cryolite forms a number of low-melting mixtures that are of significance in the formulation of fluxes.

*Reactions.* A number of acids decompose cryolite into hydrofluoric acid and the sodium and aluminum salts of the acid used; for example:

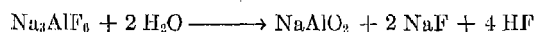


Bases react with cryolite as shown in equations (1), (2), and (3):



The reactions with lime (eq. 2 and 3) are the basis of the Thomsen wet process for caustic soda. Partial or complete replacement of sodium occurs when cryolite is heated with concentrated solutions of a number of salts.

Cryolite may be melted repeatedly in the absence of water vapor without change in composition. When heated in the presence of moist air, some decomposition occurs:



The extent of decomposition is governed by the temperature and the nature of other substances present.

The more electropositive metals react with cryolite at high temperatures, liberating aluminum. In fact, the use of sodium for this purpose was the basis of an early commercial process for aluminum production. Cryolite is reduced by magnesium also; this reaction is employed for the removal of magnesium in the refining of secondary aluminum.

#### OCCURRENCE

The only known commercial deposit of cryolite is situated at Ivigtut, Greenland. The mine is owned by the Danish State and operated by Kryolithselskabet Øresund A/S. Other occurrences, at Pikes' Peak and in the Ural Mountains, have been reported. The principal associated minerals are siderite, pyrites, galena, silica, topaz, fluorspar, ivigtite, and the hydrothermal alteration products thomsenolite, pachnolite, and hagemannite (10,16).

#### PRODUCTION

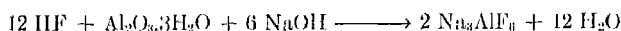
*Processing of Natural Cryolite.* Cryolite is mined by conventional open-pit methods. At the mine, a large part of the associated minerals is culled out. Purification of the imports begins with screening to remove fines in which the iron has oxidized and permanently discolored the cryolite. Further removal of impurities may be accomplished by hand-picking or magnetic separation. Cryolite is now generally refined either by flotation methods or by gravity fractionation (jigs and tables). The cryolite is finally crushed, or ball-milled and air-classified to specifications.

Metallurgical and ceramic grades of natural cryolite are designated as: "standard," 89.0-95.5% through 300-mesh; "coarse," 46-66% 80/325-mesh, 34-54% through 325-mesh; and "selected white lump," 0.5-2.5-in. pieces. Typical analyses



for sodium fluoaluminate content are as follows: standard (ceramic grade), 99.40%; selected white lump, 98.8%; metallurgical grade, 93.0%. The lump material is shipped in paper-lined wooden barrels containing 500 lb. net; the standard grade in fiber drums (400 lb.) or 5-ply paper bags (100 lb.). The insecticide grade, which contains not less than 90%  $\text{Na}_3\text{AlF}_6$  and not more than 6% silica, is 96% finer than 5 microns; it is packaged principally in 5-ply paper bags containing 50 lb.

*Synthetic Cryolite Manufacture.* A great variety of methods for the production of synthetic cryolite (4,7) have been proposed from time to time. The most successful methods, however, are based on the reaction between hydrofluoric acid or one of its derivatives (such as ammonium fluoride or fluoboric acid) and sodium aluminate (or its equivalent as hydrated alumina and alkali) (4,12):



The reactors, with appropriate stirring gear, have been lined with lead, rubber, or carbon blocks. Magnesium alloys have been found most suitable as a material of construction. Precipitation of synthetic cryolite is generally carried out at an elevated temperature (85–100°C.); heat is supplied during the initial stages, after which the heat of reaction is more than adequate to maintain the desired temperature. The product is filtered, dried, and calcined.

#### CONSUMPTION

Importation of natural cryolite declined following World War II partly as a result of a decreased demand for aluminum and partly because stock-piled ore was being utilized. Imports are therefore not at present indicative of annual consumption. Best available estimates of cryolite consumption, by use, are given in Table II. Data on the production and consumption of synthetic cryolite by the aluminum industry have not been published (see "Hydrogen fluoride," p. 695).

TABLE II. Consumption of Natural Cryolite.  
(Pounds per year, approximate)

Industry	1944	1946	1948
Aluminum reduction.....	22,500,000	14,000,000	17,000,000
Secondary aluminum.....	3,500,000	2,500,000	1,500,000
Enamels.....	2,000,000	4,500,000	2,500,000
Glass.....	2,000,000	2,500,000	2,000,000
Abrasives.....	2,500,000	2,500,000	2,500,000
Insecticide.....	12,500,000	15,000,000	<sup>a</sup>
Miscellaneous.....	300,000	700,000	1,000,000

<sup>a</sup> Data not available.

#### ANALYSIS

The ultimate analysis of natural cryolite for fluorine (18), aluminum (9), sodium (9), silica (17), calcium, and iron is accomplished by standard procedures, and from these values the mineralogical composition can be calculated. For most purposes, however, an assay of the sodium fluoaluminate content by a procedure based on the Thomsen process for caustic soda suffices. This method comprises digesting a weighed sample of cryolite with a suspension of calcium oxide (see eq. 3), removing the calcium ion from an aliquot of filtered solution by treatment with carbon dioxide, boiling, re-filtering, adding a measured excess of standard sulfuric acid, boiling to expel excess

carbon dioxide, and back-titrating the excess acid with standard sodium hydroxide solution.

In synthetic cryolite (7,9), moisture, sodium fluoride, and sodium fluosilicate must also be determined.

#### USES

The ceramic industry utilizes cryolite principally as an opacifier and as a flux in the manufacture of vitreous enamels (1) (see *Enamels*) and "opal," "alabaster," and "milk" glass (5,15). Cryolite is used in relatively small percentages in the manufacture of window and container glass because of its superior fluxing power and because it reduces the viscosity of the melt.

In the aluminum industry, cryolite is the major constituent of the electrolyte in the Hall-Héroult process for aluminum reduction (8) (see Vol. 1, pp. 592, 602). Cryolite is also used in melting and refining secondary aluminum, as a flux in the casting of aluminum alloys, and in fluxes for welding aluminum and aluminum alloys.

Cryolite is used in the production of various ferro alloys. It has also been shown to be superior to fluorspar as a flux in open-hearth operation and hence may be considered a stand-by flux for use when fluorspar is not effective in shaping up the slag. Cryolite is also used in rimming steel, where it is said to aid gas evolution.

The abrasive industry uses cryolite chiefly as a special-purpose filler in the manufacture of resin- and rubber-bonded abrasive wheels.

Cryolite has been used as an insecticide (*q.v.*) since about 1926, when its effectiveness as a substitute for arsenicals for codling moth control was demonstrated. Cryolite has since been shown to be effective against many pests (6,13).

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ISADORE MOCKRIN

### Ammonium Compounds.

**Ammonium fluoride**,  $\text{NH}_4\text{F}$ , formula weight 37.04, is a white unstable salt having a strong odor of ammonia. It decomposes above  $40^\circ\text{C}$ . with liberation of ammonia to form ammonium bifluoride. It has been reported as a sublimate in volcanic activity. At the present time the salt finds only minor commercial application.

**Ammonium bifluoride** (ammonium hydrogen fluoride, ammonium acid fluoride),  $\text{NH}_4\text{HF}_2$ , formula weight 57.05, is a white transparent solid with a slight acid odor; m.p.  $126.1^\circ\text{C}$ . (5); sublimes at higher temperatures; sp.gr. 1.211 at  $12^\circ\text{C}$ . It crystallizes in the orthorhombic system with  $a = 8.33 \text{ \AA}$ ,  $b = 8.14 \text{ \AA}$ , and  $c = 3.68 \text{ \AA}$ . The unit cell contains four  $\text{NH}_4\text{HF}_2$  groups. No hydrates of the salt are known. The salt is readily soluble in both hot and cold water, forming acid solutions. The commercial salt appears on the market as white flakes that are hygroscopic at 50% humidity and above.

Ammonium bifluoride is prepared by treating ammonia with hydrogen fluoride in approximately the proportions in which they combine to form  $\text{NH}_4\text{HF}_2$ . On cooling the resulting gaseous product below  $50^\circ\text{C}$ ., the solid product is obtained (6). Wet methods in which aqueous solutions of ammonia and hydrofluoric acid react are also used. The resultant solutions are evaporated, and the hot solution is pumped to crystallizing tanks and allowed to cool. The crystals are centrifuged dry. Several patents have been granted for the recovery of waste fluorine gases from the superphosphate industry as ammonium fluorides, but none has reached commercial production.

Ammonium bifluoride in combination with hydrofluoric acid is used extensively in the frosting of glass articles such as lamp blanks, lighting fixtures, and decorative glassware. Its solvent action is made use of in the solution of silica and silicates in analysis, the removal of scale from boilers and automobile radiators, and the treatment of oil wells. Ammonium bifluoride is used as a solvent for beryllium oxide in the preparation of beryllium metal (7) (see Vol. 2, p. 498). It is also used to remove masking materials from carburized-steel parts. Solutions of the salt are fungicidal and find use in wood preservation (4) and controlling wild yeast growth in breweries and distilleries. The salt is used to remove iron stains from cloth and has found favor as a laundry sour for the removal of excess alkali before the final rinsing (1).

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G. C. WHITAKER

### Antimony Compounds.

**Antimony trifluoride**,  $\text{SbF}_3$ , formula weight 178.76, is a white, crystalline, hygroscopic solid; m.p.  $292^\circ\text{C}$ .; b.p.  $376^\circ\text{C}$ .; sp.gr. 4.385 at  $25^\circ\text{C}$ . The solubility in water is given as 492.4 grams/100 grams water at  $25^\circ\text{C}$ ., and conductivity data indicate that

hydrolysis occurs upon dilution. Evaporation of a solution of antimony trifluoride in the absence of excess hydrogen fluoride yields the oxyfluoride. The salt is readily volatile, but sublimation in air is accompanied by some decomposition. Antimony trifluoride forms complex salts with hydrogen fluoride, antimony pentafluoride, ammonia, ammonium sulfate, and a number of metal fluorides (2). Antimony trifluoride may be prepared by the action of hydrofluoric acid on antimony trichloride or antimony trioxide,  $\text{Sb}_2\text{O}_3$ . It is used as a fluorinating agent in halogen-exchange reactions (see p. 746), for example, in the manufacture of fluorine-containing aliphatic compounds such as the Freon compounds (see p. 754). This reaction, known as the *Swarts reaction*, may employ antimony trifluoride as such, or the antimony trifluoride may be prepared *in situ* by the action of hydrofluoric acid on antimony trichloride. Addition of small amounts of pentavalent antimony salts or of chlorine may be used to promote the reaction. Antimony trifluoride is also used in the manufacture of pottery and porcelain. The complex salts of antimony trifluoride with sodium fluoride and ammonium sulfate have been used as mordants in dyeing and printing textiles.

**Antimony pentafluoride**,  $\text{SbF}_5$ , formula weight 216.76, is a hygroscopic, corrosive, oily liquid; m.p.  $7^\circ\text{C}$ .; b.p.  $149.5^\circ\text{C}$ .; sp.gr. 2.99 at  $23^\circ\text{C}$ . (2). Antimony pentafluoride may be prepared by the action of anhydrous hydrogen fluoride on antimony pentachloride or by the action of fluorine on powdered antimony metal. Antimony pentafluoride is used as such or as a mixture of antimony pentachloride with hydrogen fluoride in the preparation of organic fluorine compounds.

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F. D. LOOMIS AND C. E. INMAN

#### Barium Fluoride.

Barium fluoride,  $\text{BaF}_2$ , formula weight 175.36, forms colorless cubic crystals; m.p.  $1287^\circ\text{C}$ .; sp.gr. 4.893;  $n_D^{25}$  1.474; heat capacity, 16.98 cal./gram-mole/ $^\circ\text{C}$ . at  $27^\circ\text{C}$ . The molar heat of formation from the elements is 222.6 kg.-cal., and from aqueous barium hydroxide and hydrofluoric acid, 32.3 kg.-cal. The solubility in water is given as 1.586 grams/liter saturated solution at  $10^\circ\text{C}$ ., 1.607 at  $20^\circ\text{C}$ ., and 1.620 at  $30^\circ\text{C}$ . Barium fluoride is soluble in hydrofluoric, hydrochloric, and nitric acids and in ammonium chloride solution. It may be prepared by treating barium carbonate with hydrofluoric acid. Its principal uses are as a flux and opacifier in enamel frits and as a white pigment in phonograph record compositions. It is also used to some extent in metal heat-treating baths and in the manufacture of carbon brushes for electrical generators for aircraft.

F. D. LOOMIS

#### Beryllium Compounds.

**Beryllium fluoride**,  $\text{BeF}_2$ , formula weight 47.02, is a transparent glass, sp.gr. 1.986, that has no definite melting point but is fluid at  $800^\circ\text{C}$ . Volatilization occurs at temperatures above  $800^\circ\text{C}$ . It is soluble in water in all proportions and is also

appreciably soluble in 90% ethyl alcohol. The basic fluoride  $2\text{BeO} \cdot 5\text{BeF}_2$  is formed when an aqueous solution is evaporated. Beryllium fluoride is produced by the thermal decomposition, at  $900\text{--}950^\circ\text{C}$ ., of the *ammonium fluoberyllate*,  $(\text{NH}_4)_2\text{BeF}_4$ , produced by treating beryllium oxide with a solution of ammonium bifluoride. It is used in the production of metallic beryllium (see Vol. 2, pp. 496–98).

Other **fluoberyllates** (fluoroberyllates) such as potassium fluoberyllate and sodium fluoberyllate are also known.

F. D. LOOMIS

### Bismuth Compounds.

**Bismuth trifluoride**,  $\text{BiF}_3$ , formula weight 266.00, is formed as a gray crystalline (hexagonal) powder, sp.gr. 5.32, that melts at  $727^\circ\text{C}$ . and volatilizes at higher temperatures. It is insoluble in and unhydrolyzed by water but dissolves, with reaction, in hot hydrochloric, sulfuric, or nitric acid. It may be prepared by treating bismuth subcarbonate with aqueous hydrofluoric acid. Bismuth trifluoride absorbs fluorine at  $460\text{--}500^\circ\text{C}$ . to form the pentafluoride. No commercial uses have been developed for the trifluoride, but there is evidence that it has catalytic properties.

**Bismuth pentafluoride**,  $\text{BiF}_5$ , formula weight 304.00, is a gray crystalline (rhombohedral) material that has a sublimation point of about  $550^\circ\text{C}$ . No commercial uses have been developed.

F. D. LOOMIS

### Boron Compounds.

#### Boron Trifluoride.

Boron trifluoride,  $\text{BF}_3$ , formula weight 67.82, is a colorless gas in a dry atmosphere, but it fumes in the presence of moisture, producing a dense white smoke. Upon hydrolysis, it yields an acidic pungent odor that is irritating but not appreciably toxic. It is used widely as an acidic catalyst for many types of organic reactions, most common of which are polymerizations, esterifications, and alkylations.

The extensive research on the preparation of acetals using boron trifluoride as a catalyst, conducted by Nicuwlund in the early 1930's, aroused interest in this catalyst, and numerous new reactions were observed to be catalyzed by boron trifluoride. As a consequence, in 1932 the Harshaw Chemical Company began to investigate the possibility of the commercial production of boron trifluoride and, four years later, began to produce it on a commercial scale.

#### PHYSICAL AND CHEMICAL PROPERTIES

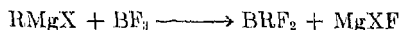
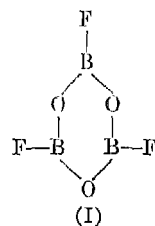
*Constants.* M.p.,  $-127.1^\circ\text{C}$ .; b.p.,  $-100.3^\circ\text{C}$ .;  $d_4^{-100.3}$  (liquid), 1.57;  $d_4^{-127.1}$  (liquid), 1.68; apparent density, 3.07666 grams/liter;  $n_D^{20}$ , 1.0004134; vapor pressure (liquid) at  $146.0\text{--}172.8^\circ\text{K}$ .,  $\log p$  (in mm.) =  $-1174.4/T + 1.75 \log T - 0.013350T + 8.0536$ , at  $199.8\text{--}260.8^\circ\text{K}$ .,  $\log p$  (in atm.) =  $5.1009 - 889.6/T$ ; surface tension at  $-116.4$  to  $-92.6^\circ\text{C}$ .,  $\gamma$  (in dynes/cm.) =  $20.92 - 0.22(t + 117.0)$ , where  $t = ^\circ\text{C}$ .; parachor, 87.3; heat of fusion, 1.0138 kg.-cal./gram-mole; heat of vaporization, 4.440 kg.-cal./gram-mole; entropy at  $298.2^\circ\text{K}$ ., 61.17 cal./(gram-mole)( $^\circ\text{K}$ .); heat of soln., 24.5 kg.-cal./gram-mole; heat of formation, 256.9 kg.-cal./gram-mole; crit. temp.,  $-12.25^\circ\text{C}$ .; crit. pressure, 49.2 atm. For other constants, see reference (3).

Boron trifluoride dissolves in water to the extent of 322.1 grams/100 grams of water at 0°C. and 762 mm. Hg. One volume of boron trifluoride is soluble in 50 volumes of sulfuric acid (sp.gr. 1.85). It is also soluble in concentrated nitric acid. It dissolves in ethane, propane, pentane, kerosene, high-boiling naphtha, carbon disulfide, carbon tetrachloride, chloroform, tetrachloroethane, benzene, nitrobenzene, dichlorobenzene, and terebene. Quantitative data are lacking except for *n*-pentane (6).

**Reactions.** Boron trifluoride reacts with incandescence when heated with alkali or alkaline earth metals. Molten magnesium and its alloys, however, do not react. Neither gaseous nor liquid boron trifluoride, at room temperature or below, reacts with mercury or chromium plate, even when subjected to pressure for a considerable length of time. Boron trifluoride is reported not to react with red-hot iron. When reduced with hydrogen gas in a tungsten arc, crystalline boron is obtained.

Alkali and alkaline earth metal oxides react with boron trifluoride to form the borate and fluoborate. Boric oxide and boron trifluoride are reported to react at 450°C. to form the volatile sublimate *boron oxyfluoride*,  $(\text{BOF})_3$ . It is postulated that this compound has the structure shown in formula (I). This trimer is also obtained when boron trifluoride reacts with potassium metaborate, potassium nitrate, potassium carbonate, dolomite, titania, alumina, silica, magnesia, calcium oxide, lithium carbonate, magnesium silicate, calcium silicate, glass, kaolin, feldspar, or oligoclase (1).

Boron trifluoride and  $\beta$ -diketones (for example, acetylacetone and benzoylacetone) split out hydrogen fluoride to form substituted difluorides such as  $\text{CH}_3\text{COCH}:\text{C}(\text{CH}_3)\text{OBF}_2$  and  $\text{C}_6\text{H}_5\text{COCH}:\text{C}(\text{CH}_3)\text{OBF}_2$ . Trialkylborines may be prepared by treating a zinc alkyl, an alkylaluminum halide, or an alkylmagnesium halide with boron trifluoride. Triarylborines may be obtained by use of an arylmagnesium halide.



An excess of boron trifluoride yields mono- and difluoro derivatives. Diborane,  $\text{B}_2\text{H}_6$ , is formed by the reaction of the ethyl etherate of boron trifluoride and lithium hydride or lithium or sodium borohydride (see Vol. 2, p. 593). In ethylamine, lithium reacts with boron trifluoride to produce boron triethylimine,  $\text{B}(\text{C}_2\text{H}_5\text{NH})_3$ . Methylboron difluoride and dimethylboron fluoride are obtained when methylboron oxide,  $(\text{CH}_3\text{BO})_3$ , and dimethylboron oxide,  $((\text{CH}_3)_2\text{B})_2\text{O}$ , respectively, are treated with boron trifluoride.

Boron trifluoride, being an electron-deficient molecule, is strongly electrophilic and consequently easily forms many molecular compounds with electrodotic molecules (molecules having at least one unshared pair of electrons). As would be expected from the characteristic properties of metals, no elements in Groups I, II, or III of the periodic table have been reported to donate an electron pair to boron trifluoride. No molecular compounds have been isolated in which the carbon atom is the donor. It is postulated, however, that intermediate molecular compounds in which carbon is electrodotic are formed in certain organic reactions in which boron trifluoride serves as a

catalyst, for example with isobutene,  $(\text{CH}_3)_2\text{C}^+-\text{CH}_2 \rightarrow \text{BF}_3$ . No other elements in Group IV have been reported to act as donor atoms toward boron trifluoride.

Nitrogen compounds readily form molecular compounds with boron trifluoride. Ammonia; primary, secondary, and tertiary amines; aniline and alkyl-substituted anilines; pyridine; hydrogen cyanide; and nitriles readily form one-to-one compounds with boron trifluoride. Phosphine forms two compounds,  $\text{PH}_3\cdot\text{BF}_3$  and  $\text{PH}_3\cdot 2\text{BF}_3$ . Arsenic has not been reported as a donor to boron trifluoride.

Oxygen, in either inorganic or organic molecules, forms many compounds with boron trifluoride, whereas sulfur has been reported to form only a few. Boron trifluoride forms three hydrates,  $\text{BF}_3\cdot\text{H}_2\text{O}$ ,  $\text{BF}_3\cdot 2\text{H}_2\text{O}$ , and  $\text{BF}_3\cdot 3\text{H}_2\text{O}$ . With oxides and hydroxides, it forms compounds such as  $\text{NaOH}\cdot\text{BF}_3$ ,  $\text{KOH}\cdot\text{BF}_3$ ,  $\text{NO}\cdot\text{BF}_3$ , and  $\text{B}_2\text{O}_3\cdot\text{BF}_3$ . Sulfuric, nitric, orthophosphoric, and pyrophosphoric acids, as well as salts of these acids, coordinate with boron trifluoride, for example,  $\text{Na}_2\text{SO}_4\cdot\text{BF}_3$ ,  $\text{Cs}_2\text{SO}_4\cdot 2\text{BF}_3$ ,  $\text{K}_3\text{PO}_4\cdot 3\text{BF}_3$ , and  $\text{Na}_4\text{P}_2\text{O}_7\cdot 4\text{BF}_3$ .

Most of the coordination compounds reported to be formed by boron trifluoride are with oxygen-containing organic molecules. Whereas the other boron halides readily react with these types of organic molecules to split out hydrogen halide, boron trifluoride (due to the strong boron-to-fluorine bond) normally does not split out hydrogen fluoride, but forms stable molecular compounds. The major classes of organic molecules which serve as donors, along with a few typical examples, follow.

*Alcohols:*  $\text{C}_2\text{H}_5\text{OH}\cdot\text{BF}_3$ ;  $2\text{C}_2\text{H}_5\text{OH}\cdot\text{BF}_3$ ;  $2\text{ClCH}_2\text{CH}_2\text{OH}\cdot\text{BF}_3$ ;  $2\text{Cl}_2\text{CHCH}_2\text{OH}\cdot\text{BF}_3$ ;  $2\text{C}_6\text{H}_5\text{CH}_2\text{OH}\cdot\text{BF}_3$ .

*Acids:*  $\text{CH}_3\text{COOH}\cdot\text{BF}_3$ ;  $2\text{CH}_3\text{COOH}\cdot\text{BF}_3$ ;  $\text{C}_6\text{H}_5\text{COOH}\cdot\text{BF}_3$ ;  $2\text{C}_6\text{H}_5\text{OH}\cdot\text{BF}_3$ ;  $(\text{COOH})_2\cdot\text{BF}_3$ .

*Ethers:*  $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{BF}_3$ ;  $\text{CH}_3\text{OC}_2\text{H}_5\cdot\text{BF}_3$ ;  $\text{CH}_3\text{OC}_6\text{H}_5\cdot\text{BF}_3$ .

*Acid anhydrides:*  $(\text{CH}_3\text{CO})_2\text{O}\cdot\text{BF}_3$ ;  $(\text{CH}_2\text{CO})_2\text{O}\cdot\text{BF}_3$ ;  $((\text{CH}_3\text{CO})_2\text{CHCO})_2\text{O}\cdot 3\text{BF}_3$ .

*Esters:*  $\text{HCOOC}_2\text{H}_5\cdot\text{BF}_3$ ;  $\text{CH}_3\text{COOC}_6\text{H}_5\cdot\text{BF}_3$ ;  $\text{CH}_3\text{COOC}_6\text{H}_4\text{CH}_3(p)\cdot\text{BF}_3$ .

*Ketones:*  $(\text{CH}_3)_2\text{CO}\cdot\text{BF}_3$ ;  $\text{C}_6\text{H}_5\text{COCH}_2\text{COCH}_3\cdot\text{BF}_3$ .

*Aldehydes:*  $\text{CH}_3\text{CHO}\cdot\text{BF}_3$ ;  $(\text{CH}_3)_3\text{CCHO}\cdot\text{BF}_3$ ;  $\text{Cl}_3\text{CCHO}\cdot\text{BF}_3$ .

Hydrogen sulfide, sulfur dioxide, and thionyl fluoride have been found to form one-to-one molecular compounds with boron trifluoride. The only organic molecules reported to form molecular compounds through sulfur with boron trifluoride are alkyl sulfides and mercaptans.

Compounds containing fluorine, chlorine, and bromine from Group VII have been studied as donors to boron trifluoride. Three solvates with hydrogen fluoride have been reported, namely,  $\text{BF}_3\cdot\text{HF}$ ,  $\text{BF}_3\cdot 2\text{HF}$ , and  $\text{BF}_3\cdot 3\text{HF}$ . Fluoboric acid and the fluoborates of metals, nonmetals, and organic radicals represent a large class of compounds in which a fluoride ion is coordinating with boron trifluoride. Representative examples of these compounds are  $\text{KBF}_4$ ,  $[\text{Ni}(\text{NH}_3)_6][\text{BF}_4]_2$ ,  $\text{NOBF}_4$ ,  $\text{CH}_3\text{COBF}_4$ ,  $(\text{CH}_3)_3\text{OBF}_4$ , and  $\text{C}_5\text{H}_5\text{N}(\text{C}_2\text{H}_5)\text{BF}_4$ .

Although hydrogen chloride does not coordinate with boron trifluoride, its salts do. Coordination compounds of boron trifluoride with the chlorides of sodium, aluminum, iron, copper, zinc, tin, and lead have been indicated. Hydrogen bromide, like hydrogen chloride, does not coordinate with boron trifluoride.

In Group 0, argon has been found to form under pressure and at low temperatures six molecular compounds with boron trifluoride, namely,  $\text{A}\cdot\text{BF}_3$ ,  $\text{A}\cdot 2\text{BF}_3$ ,  $\text{A}\cdot 3\text{BF}_3$ ,  $\text{A}\cdot 6\text{BF}_3$ ,  $\text{A}\cdot 8\text{BF}_3$ , and  $\text{A}\cdot 16\text{BF}_3$ .

## ANALYSIS

There is no direct, simple, qualitative analytical procedure for the determination of boron trifluoride. Boron trifluoride may be detected by spectrographic analysis. The results so obtained are sensitive to one part per thousand and check the results obtained by chemical methods (5).

Acetyl fluoride and boron trifluoride react quantitatively to yield acetyl fluoborate. The common contaminant of boron trifluoride, silicon tetrafluoride, does not react with acetyl fluoride, and the presence of as little as 0.2% silicon tetrafluoride has been detected thus (15). Boron trifluoride may be absorbed by an aqueous solution of sodium fluoride to form sodium fluoborate, which can be detected by the usual procedures.

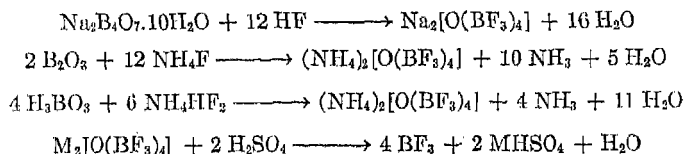
Recently, an excellent procedure for sampling and making a complete analysis of gaseous boron trifluoride has been reported (18). After the water-soluble components have been absorbed in an aqueous solution of sodium chloride, air is determined in a gas buret. Sulfur dioxide must be the first water-soluble component determined, because it may be lost upon standing. The sulfur dioxide is determined on an aliquot by use of standardized iodide-iodate and thiosulfate solutions. The silicon tetrafluoride and the boron trifluoride in a second aliquot are converted to sodium fluosilicate and fluoborate. The fluosilicate is titrated with standardized sodium hydroxide and the equivalent of silicon tetrafluoride calculated. A third aliquot is treated with a neutral solution of calcium chloride, and then the total acidity is determined with standard alkali to the methyl orange end point. Inasmuch as no other acidic gases are normally present in commercial boron trifluoride, deduction of the above-determined quantities of sulfur dioxide and silicon tetrafluoride leaves the amount of boron trifluoride present. Subsequent titration in the presence of mannitol to the phenolphthalein end point will give the amount of boron present, if desired.

Organic molecular complexes with boron trifluoride may be analyzed by addition of an accurately weighed quantity of sodium fluoride and refluxing for one-half hour to form sodium fluoborate. The organic constituent (b.p. 200°C. or less) is then distilled off, and from the gain in weight of the residue the quantity of boron trifluoride is ascertained to within 0.5% (19).

Another procedure involves the ignition of the molecular compound formed between an organic molecule and boron trifluoride in a Parr sulfur bomb. The fluoride is determined gravimetrically as calcium fluoride and the boron volumetrically with standard caustic in the presence of mannitol (16).

## MANUFACTURE

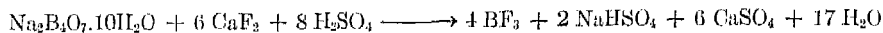
Commercially, boron trifluoride is produced by treating borax with hydrogen fluoride, or boron oxide or boric acid with ammonium fluoride or bifluoride, to form, respectively, an intermediate compound,  $\text{Na}_2[\text{O}(\text{BF}_3)_4]$  or  $\text{Na}_2\text{O} \cdot 4\text{BF}_3$  (sodium "fluoborax"), or  $(\text{NH}_4)_2[\text{O}(\text{BF}_3)_4]$  or  $(\text{NH}_4)_2\text{O} \cdot 4\text{BF}_3$  (ammonium "fluoborax"). The intermediate compound is treated with fuming sulfuric acid (20%  $\text{SO}_3$ ) and heated to liberate boron trifluoride as follows (21,22):



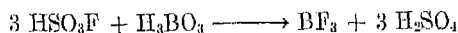


The evolved gas is passed through cooling towers to remove spray, and then stored in gasholders until compressed into steel cylinders.

An older commercial process involved the reaction of borax, fluorspar, and sulfuric acid:



From the equations it may be seen that two and eight moles of sulfuric acid are required as a reactant for the newer and older processes, respectively. In addition, one and seventeen moles of sulfuric acid are required as a desiccant in the respective processes (counting one mole of sulfuric acid for one mole of water). Therefore, to produce four moles of boron trifluoride, the newer and older processes require three and twenty-five moles of sulfuric acid, respectively. Another commercial method of producing boron trifluoride is treating fluosulfonic acid with boric acid (23).



There are types of reactions too numerous to mention for the production of small quantities of boron trifluoride, for some of which a product of high purity is claimed.

#### PURITY AND SAFETY FACTORS

Commercial boron trifluoride is usually about 99% pure. The common impurities are silicon tetrafluoride, sulfur dioxide, and air, with traces of hydrogen, sulfur trioxide, hydrogen fluoride, and moisture. Higher purity may be attained by fractional distillation.

A high concentration of boron trifluoride will burn the skin, similarly to, but less severely than, hydrogen fluoride. The burns should be treated similarly. Inhalation of boron trifluoride irritates the respiratory tract. The toxicity of the gas to man has not been reported, but to date no medical evidence has been reported for any chronic effects among workers exposed to small quantities of the gas at frequent intervals over a period of eight years.

The gas is shipped in steel cylinders under a pressure of 1800 p.s.i. Cylinders containing from 2 to 60 lb. of the gas may be obtained. It is compressed with oil as a lubricant and therefore must not be used with oxygen under pressure nor with gages, valves, or lines which are to be used with oxygen.

Inasmuch as the gas readily hydrolyzes, all equipment should be rinsed about ten times with dry air before admitting boron trifluoride. If the gas is to be handled under anhydrous conditions, steel equipment is most satisfactory. At low pressures and temperatures, malleable iron, copper, brass, or glass may be used. For temporary low-pressure connections, rubber pressure tubing may be employed. If used for any length of time, the rubber tubing becomes hard, brittle, and unreliable. Neoprene is more resistant than natural rubber.

If moisture is present, boron trifluoride may be handled in copper, Saran, hard rubber, paraffin wax, polyethylene, or glass containers. Iron is but slightly attacked. If the situation will permit, corrosion of the equipment may be minimized by diluting the boron trifluoride with a gas inert to the reactants. Nitrogen and carbon dioxide are inert toward boron trifluoride.

Litharge and oil or soft Vistanex No. 6 when dissolved in carbon tetrachloride (with or without graphite) serve as good pipe-joint compounds. Bar stock valves are good flow-regulating valves and should be attached to the cylinder valve, inasmuch as the cylinder valve is an emptying and not a control valve. The Kerotest cylinder

valve is especially constructed so that in the closed position the entire stem and packing material may be removed and replaced while the cylinder is under pressure. Special instructions for the use of the Kerotest valve accompany each cylinder. The stem of a bar stock valve is suitably packed as supplied. Asbestos with graphite and oil (Garlock No. 115) is a suitable packing. Saran and Teflon serve as satisfactory gasket materials. Materials containing rubber, fiber, polymerizable materials, or organic oxygen- and nitrogen-containing compounds are attacked by boron trifluoride and must be avoided in packing or gasket materials. Mercury, carbon tetrachloride, white mineral oil, and petroleum spirits (mineral spirits, A.S.T.M. D235-39) are suitable confining liquids for flowmeters, vacuum breaks, manometers, gasholders, etc.

Boron trifluoride reacts with water, ammonia, and organic molecules containing oxygen or nitrogen, such as alcohols, amines, acids, and esters. Therefore, the gas must not be introduced into these liquids, unless a vacuum break or similar safety device is employed.

#### USES

Boron trifluoride was made available commercially after it had been shown that it was an excellent catalyst for numerous organic reactions. Since then the use of boron trifluoride as a catalyst has been the subject of many research programs, with the result that approximately seven hundred patents have been issued in this field alone. These patents cover the use of boron trifluoride as a catalyst for: the synthesis of saturated hydrocarbons, olefins, alcohols, mercaptans, ketones, and ethers; carbon monoxide addition reactions; esterifications, involving condensations of acids with acetylene, olefins, and alcohols; decomposition reactions such as the cracking of hydrocarbon oils; hydrations; dehydration of alcohols, acids, and ketones; hydrogenations and reductions; oxidations such as the conversion of benzaldehyde to benzoic acid; sulfonations; nitrations; halogenations; alkylations using olefins, alcohols, ethers, and esters as alkylating agents; acylations; polymerizations of olefins, vinyl compounds, dienes, terpenes, heterocyclic compounds, and cyclic oxides; and isomerizations such as the Beckmann rearrangement, the benzidine transformation, the rearrangements of phenyl acetate to *p*-hydroxyacetophenone and of diazoaminobenzene to aminoazobenzene. See also *Friedel-Crafts reaction*.

Boron trifluoride has been used in catalysis in many different ways and under a great variety of conditions. It may be used alone in the gas phase or in the presence of promoters, such as: metallic nickel; oxides of nickel, mercury, and zirconium; oxygen-containing compounds of aluminum, silicon, titanium, vanadium, chromium, manganese, iron, cobalt, and nickel; silica gel; and activated carbon.

Frequently, boron trifluoride is used in the presence of inorganic chemicals with which it forms molecular compounds. Among the more commonly used compounds are water, hydrogen fluoride, sulfuric acid, fluosulfonic acid, dihydroxyfluoboric acid,  $\text{H}[\text{B}(\text{OH})_2\text{F}_2]$ , and ortho- and pyrophosphoric acids. In still other catalyses, coordination compounds of boron trifluoride with organic chemicals are used. The commercially available boron trifluoride ethyl etherate and phenolate are most commonly used.

Boron trifluoride is frequently recovered after it has been used as a catalyst. This may be accomplished by distillation methods, by chemical reactions, or a combination of the two. Frequently, ammonia or amines are added to the spent catalyst to form with it stable coordination compounds which can be separated from the reaction products. Subsequent treatment of the coordination compound with sulfuric acid re-

leases the boron trifluoride. An organic compound may be added that will form a more stable molecular compound than that formed by the desired product and boron trifluoride. By so doing, the desired product is liberated and the boron trifluoride recovered later from the more stable coordination compound. Another procedure frequently employed involves the addition of a fluoride to the reaction products to precipitate the boron trifluoride as an insoluble compound. Subsequent heating releases the boron trifluoride. Selective solvents may also be employed in recovery procedures.

In addition to its major application as a catalyst, boron trifluoride has been used to protect molten magnesium and its alloys from oxidation during casting, and as a flux for soldering magnesium (20). Boron trifluoride is employed in the synthesis of the other boron halides by reaction with the appropriate aluminum halide (8).

Organoboron compounds are synthesized cheaply by using a Grignard reagent and boron trifluoride (12). Boron trifluoride has been suggested as a fumigant, displaying a high toxicity for insects such as grain weevils, bean weevils, bedbugs, and roaches (13). Boron trifluoride is employed in ionization chambers for the detection of weak neutron sources (17).

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D. R. MARTIN

### Fluoboric Acid.

Fluoboric acid (tetrafluoroboric acid, borofluoric acid),  $\text{HBF}_4$ , formula weight 87.83, has not been prepared in anhydrous condition, although mixtures of hydrogen fluoride and boron trifluoride approximating  $\text{HBF}_4$  in composition have been made and utilized industrially. The acid is known in the form of colorless aqueous solutions.

Fluoboric acid was discovered in 1809 by Gay-Lussac and Thénard, who prepared the acid by passing an excess of boron trifluoride into cold water. Its chief industrial applications include its use as a catalyst in a variety of organic reactions and as a constituent of electrolytes used in metal plating.

**Other Fluoboric Acids.** Of the other fluoboric acids known as such or as their salts (1),  $\text{H}_2\text{BF}_3$ ,  $\text{H}_2\text{B}_2\text{F}_6$ ,  $\text{H}_4\text{B}_4\text{F}_{10}$ ,  $\text{H}_2\text{BO}_2\text{F}$ ,  $\text{H}_2\text{BO}_2\text{F}_2$ ,  $\text{H}_2\text{B}_2\text{O}_3\text{F}_3$ ,  $\text{H}_2\text{B}_2\text{O}_4\text{F}_2$ ,  $\text{H}_2\text{B}_2\text{O}_5\text{F}_1$ ,  $\text{H}_4\text{BO}_2\text{F}_3$ ,  $\text{H}_4\text{BO}_3\text{F}_3$ ,  $\text{H}_4\text{B}_4\text{O}_{11}\text{F}_4$ ,  $\text{H}_6\text{B}_2\text{O}_9\text{F}_2$ ,  $\text{H}_7\text{B}_3\text{O}_7\text{F}_3$ ,  $\text{H}_{14}\text{B}_4\text{O}_7\text{F}_{16}$ , and  $\text{H}_4\text{BO}_2\text{F}_2$ , the last-named, "dihydroxyfluoboric acid," is the most important. It is prepared by absorbing anhydrous hydrogen fluoride in a solution of boric acid in an ice-cooled reactor or by treating boron trifluoride with boric acid. The acid is a colorless, sirupy liquid; m.p.,  $4.0-4.5^\circ\text{C}$ .;  $b_{760}$ ,  $159-160^\circ\text{C}$ .;  $b_{16}$ ,  $84-86^\circ\text{C}$ .;  $d_{4}^{25}$ , 1.6560;  $n_D^{25}$ , 1.3323. It fumes in moist air, but does not attack glass. It has been used commercially as a catalyst, especially in alkylation and esterification (2,6). A better name for this acid is considered to be "difluoboric acid."

**Properties.** The boiling points of fluoboric acid solutions lie above  $100^\circ\text{C}$ . Commercial acid (42%) has a specific gravity of 1.31-1.33; the 78% acid has a specific gravity of 1.77. The refractive index of a 20% acid is given as 1.3284 at  $20^\circ\text{C}$ . Heats of formation have been reported as follows: from the elements and water, 388.5 kg.-cal./gram-mole; from boron trifluoride and water,  $21.9 \pm 0.2$  kg.-cal./gram-mole of  $\text{BF}_3$  at  $0^\circ\text{C}$ .; from glassy boric acid and 3.65% hydrofluoric acid, 29.64 kg.-cal./gram-mole of  $\text{H}_3\text{BO}_3$  dissolved; and from aqueous boric oxide and hydrofluoric acid, 29.479 kg.-cal./gram-mole.

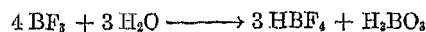
Fluoboric acid is considered a strong acid. Ionization may be followed by very limited dissociation of the fluoborate ion. In aqueous solution, fluoboric acid is hydrolyzed to "monohydroxyfluoboric acid,"  $\text{H}[\text{BF}_3\text{OH}]$ , and hydrofluoric acid to the extent of 5.50% in a 5.41 molar solution, 7.98% in a 0.557 molar solution, 18.7% in a 0.0504 molar solution, and 46.3% in a 0.00509 molar solution (12). Further stepwise hydrolysis has also been postulated.

Fluoboric acid behaves normally as a monobasic acid with metals, oxides, hydroxides, and carbonates, forming metal fluoborates. Concentrated solutions of the acid will dissolve silica and attack glass, dilute solutions will not.

**Analysis.** Fluoboric acid or its soluble salts can be detected qualitatively by precipitation of the potassium salt or as nitron fluoborate. The quantitative analysis of these materials is complicated by the lack of a sufficiently insoluble salt. The usual procedure involves the hydrolysis of the fluoborate ion in the presence of calcium ion with either a subsequent determination of the fluorine and the boron as such, or of the fluoborate content on the basis of alkali consumed by the hydrolysis. The hydrolysis of the fluoborate ion even on the steam bath is relatively slow and must be complete for accurate results by either technique. If the fluorine and the boron are determined as such, the general procedure to be followed is as given by Treadwell and Hall (11). For commercial products, the amounts of probable impurities, such as sulfuric acid, sulfates, boric acid, hydrofluoric acid, and fluosilicic acid, must be determined separately and suitable corrections made before calculating the fluoboric acid according to the method given by Booth and Martin (1).

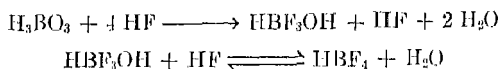
The analysis of fluoborate salts for metallic ion content can be performed by fuming with sulfuric acid, thereby converting to the metal sulfate.

**Manufacture.** Fluoboric acid may be prepared by dissolving boron trifluoride in water. The rate of absorption is high and precautions must be taken to prevent the water from siphoning back into the boron trifluoride generator or cylinder.



The saturation solubility of boron trifluoride has been reported as 1057 ml. (3.220 grams) per milliliter of water at 0°C. and 762 mm., and 700 ml. per milliliter of water at 10°C. and 762 mm. pressure. These solubilities calculate to fluoboric acid concentrations of 90% and 78%, respectively, after removing the boric acid.

Commercially, fluoboric acid is generally produced by dissolving boric acid in concentrated hydrofluoric acid:



Theoretically, the concentrations of fluoboric acid obtainable from 40%, 50%, and 60% hydrofluoric acid are 33%, 40%, and 45%, respectively; commercial fluoboric acid averages 42%. The reaction is carried out in lead-, impregnated-carbon-, or, preferably, rubber-lined tanks, provided with stirrers and cooling coils to maintain a temperature below about 40°C. Little heat is evolved upon initial mixing, but as the reaction proceeds the temperature suddenly rises and continues to rise unless the mixture is cooled.

Fluoboric acid has also been prepared by the interaction at 70–100°C. of fluorspar, sulfuric acid, and boric acid (15); by treating barium fluoborate with sulfuric acid (10); and by the thermal decomposition of ammonium fluoborate vapors at 600°C. or higher and absorption of the resulting fluoboric acid in water (18). The last-named method reportedly yields an acid of 80–85% concentration.

**Hazards.** Fluoboric acid and its salts, like all soluble fluorine compounds, are poisonous. Ingestion of these compounds and inhalation of their vapors or dusts must be avoided. While the acid and its salts are much less corrosive than hydrofluoric acid, they should be handled with the same precautions observed in working with the common acids.

**Uses.** The commercial development of boron trifluoride, fluoboric acid, and its other derivatives is largely attributable to the value of these compounds as catalysts in a wide variety of organic reactions (1). It is claimed that in many instances the use of fluoboric acid in place of boron trifluoride permits better control of the reaction.

Fluoboric acid is used for the preparation of metal fluoborates. Both the acid and its salts are used in electroplating baths (9). Fluoborate electrolytes are now accepted in lead and tin-lead plating; increasing interest in their use for tin, cadmium, copper, and indium plating is credited to very high anode and cathode efficiencies, high conductivity, simplicity of operation at room temperature, and better fine-grain deposits (8). Fluoboric acid is also used in the cleaning of metal preparatory to plating.

Fluoboric acid has been used in the preparation of diazonium fluoborates, which are of value as a means of producing aryl fluorides. It has also been used to treat magnesium and its alloys to preserve the surface (16,17) and as a constituent of molding compositions for casting magnesium (14).

### Metal Fluoborates

The fluoborates have been found in nature only in trace amounts, among the products of volcanic activity. They were first synthesized by Gay-Lussac and Thénard, but the major part of the early work on these salts was done by Berzelius. The potassium, rubidium, and cesium salts are sparingly soluble in water and are precipitated when fluoboric acid is treated with a salt of the appropriate metal. The lithium, sodium, ammonium, alkaline earth, and heavy-metal salts are soluble; in the

majority of cases they may be crystallized from solutions obtained by neutralizing fluoboric acid with the appropriate hydroxide or carbonate (1,4,13).

Ammonium, sodium, and potassium fluoborates are available commercially as white crystalline (orthorhombic) solids. Table I gives some of their properties.

TABLE I. Properties of Metal Fluoborates.

Property	NH <sub>4</sub> BF <sub>4</sub>	NaBF <sub>4</sub>	KBF <sub>4</sub>	RbBF <sub>4</sub>	CsBF <sub>4</sub>
Formula wt.	104.86	109.82	125.92	172.30	219.73
M.p., °C.	230	384 (dec.)	529.5	590	550
d <sub>4</sub> <sup>20</sup>	1.85 <sup>17.5</sup>	2.47	2.50	2.82	3.2
Soly., g./100 g. H <sub>2</sub> O	20.3 <sup>23</sup> 97 <sup>100</sup>	109 <sup>20.5</sup> 218 <sup>100</sup>	0.448 <sup>20</sup> 6.27 <sup>100</sup>	0.6 <sup>17</sup> 10 <sup>100</sup> (approx.)	1.6 <sup>17</sup> 30 <sup>100</sup> (approx.)

*Potassium fluoborate* is made by treating fluoboric acid with potassium carbonate, hydroxide, nitrate, chloride, or sulfate. It melts without decomposition, but dissociates into potassium fluoride and boron trifluoride before reaching its boiling point. It is decomposed by sulfuric acid into potassium sulfate, hydrogen fluoride, boric acid, and boron trifluoride. On the other hand, sulfur trioxide forms a solid addition product, KBF<sub>4</sub>·4SO<sub>3</sub>, which decomposes at 130°F. to potassium fluosulfonate. The sulfur trioxide addition product is an active sulfonating agent. Potassium fluoborate is not attacked by dilute alkali solutions, but is converted to the fluoride and borate by alkali fusion. It has been suggested as an ingredient of brazing and soldering fluxes.

*Sodium fluoborate* is prepared in a manner analogous to that used for the potassium salt. It has been used in the heat treatment of aluminum alloys to prevent blistering and crack formation. The alkali metal fluoborates in general have been suggested as grain-refining agents and purifying fluxes for nonferrous metals, especially aluminum.

*Ammonium fluoborate* is prepared by fusing ammonium fluoride with boric acid or boric oxide, or by neutralizing fluoboric acid with ammonia. It may be purified by sublimation. It is used as a core spray or molding-sand additive in magnesium casting to inhibit oxidation. It has also been proposed as a catalyst in making aminotriazine-aldehyde (melamine-aldehyde) resin adhesives.

The other metal fluoborates available commercially are sold in the form of solutions, especially formulated for use in electroplating, and contain 40-50% of the salt and small amounts of free fluoboric and boric acids (8).

*Lead fluoborate* is of particular interest because it may be used to plate directly onto steel or cast iron to give an acid-resistant coating for containers or a noncorrosive surface for bearings. It is made from lead carbonate, boric acid, and hydrofluoric acid.

Solutions of *other fluoborates* (cadmium, zinc, iron, chromium, copper, indium, nickel, and silver) have also been produced commercially (9).

### Organic Fluoborates

Six classes of organic fluoborates have been reported: (1) the alkyl- and aryl-ammonium fluoborates typified by tetramethylammonium fluoborate and pyridinium fluoborate, (2) carboxonium fluoborates such as acetyl fluoborate, (3) triphenylmethyl fluoborate, (4) tertiary oxonium fluoborates such as triethyloxonium fluoborate, (5) tetraalkylammonium triphenylfluoborates (3a), and (6) diazonium fluoborates. At the present time, the diazonium fluoborates are of importance because they afford a means of combining the fluorine atom directly with an organic nucleus. When aniline

is diazotized in the presence of fluoboric acid, 90–97% yields of benzenediazonium fluoborate are produced (3). Thermal decomposition of the latter compound gives fluorobenzene in 70–80% yield, nitrogen, and boron trifluoride.

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**Bromine Compounds.** See under "Halogen fluorides," p. 694.

### Cadmium Fluoride.

Cadmium fluoride,  $\text{CdF}_2$ , formula weight 150.41, forms white cubic crystals; m.p.  $520^\circ\text{C}$ .; sp.gr. 6.64. Its boiling point is not definitely known but is greater than  $1200^\circ\text{C}$ . It is soluble in water but is much less soluble than the other halides of cadmium. It crystallizes in the cubic system, thereby departing from the habit of the other halides. The cell has a parameter of  $a_0 = 5.40 \text{ \AA}$ .

The salt may be made by dissolving cadmium in a solution of hydrogen fluoride and evaporating to dryness. It may also be made by the addition of ammonium fluoride to a solution of the chloride.

Cadmium fluoride, along with other metal fluorides, has been studied as a fluorinating agent in the vapor-phase conversion of  $\alpha, \alpha, \alpha$ -trichlorotoluene to  $\alpha, \alpha, \alpha$ -trifluorotoluene (benzotrifluoride) (3). Cadmium fluoride may replace up to 90% of the zinc fluoride in the fluoride phosphors of cathode-ray-beam tubes. Its function is to vary the decay characteristics of the phosphor (5). Cadmium fluoride is useful for impregnating carbon brushes in dynamos, etc., to prevent excessive wear of the brushes (4).

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G. U. GREENE

### Calcium Fluoride (Fluorspar).

Calcium fluoride,  $\text{CaF}_2$ , formula weight 78.08, is a colorless crystalline (cubic) compound when pure; m.p.,  $1360^\circ\text{C}$ .;  $d_4^{20}$ , 3.180;  $n_D$ , 1.43385; solubility at  $18^\circ\text{C}$ ., 0.0016 gram per 100 grams of water. It is slightly soluble in cold strong acids and quite soluble in solutions of aluminum salts. It is not attacked by boiling solutions of sodium or potassium hydroxide, but is decomposed by hot sulfuric acid forming hydrogen fluoride and calcium sulfate. Calcium fluoride, in the form of the mineral fluorspar, is widely used in industry.

**Fluorspar**, or fluorite, belongs to the isometric crystal system; it has a vitreous luster and a perfect octahedral cleavage. It may be transparent and colorless, or translucent and white, or it may exhibit any of a wide range of colors: red, yellow, green, blue, brown, and black. In certain cases the color may be discharged by heating to  $200\text{--}300^\circ\text{C}$ . Fluorspar has a hardness of 4 on Mohs' scale. The density may vary from 3.00 to 3.25, with a mean value of 3.18. The heat capacity generally falls in the range  $0.208\text{--}0.212$  cal./( $\text{mole}$ )( $^\circ\text{C}$ ).

Fluorspar was known and recognized as a flux as early as 1529. Although several deposits of fluorspar were discovered in the United States during the period 1814–1818, the commercial utilization of this mineral did not begin until about 1880 with the advent of the basic open-hearth process. It is now used as a flux in metallurgy, as a source of fluorine in the chemical industry, and as an opacifier in the ceramic industry.

*Occurrence.* Fluorspar is a common mineral and is widely distributed in nature. Good industrial deposits are found in the United States, Germany, England, Russia, Newfoundland, France, Spain, Italy, and Mexico. In the United States, fluorspar deposits are worked chiefly in Illinois, Kentucky, New Mexico, and Colorado, with 75–80% of the U.S. production coming from the Illinois-Kentucky field.

*Mining and Processing.* Almost all types of mining methods have been used on fluorspar deposits. Surface mining, however, has gradually disappeared as the more accessible deposits have been worked out. Today, underground mining is used almost exclusively, shaft and tunnel operations being most common.

Fluorspar is generally associated with varying quantities of limestone, calcite, barite, quartz, sphalerite, galena, pyrite, and chalcopyrite. The amounts of these impurities must be reduced to meet the specifications for the several grades marketed. The methods of beneficiating crude ore vary greatly; the following, however, may be considered a typical process (see also reference (1)). The crude ore is crushed, water-washed, and fed mechanically to an endless belt where No. 1 and No. 2 high-grade lump, and coarse waste are picked off by hand. The high-grade spar from the picking belt may be shipped as such or subjected to additional mill treatment. The material from the end of the picking belt is further beneficiated by gravity concentration (*q.v.*) on jigs and tables, and by flotation (*q.v.*). The flotation process, developed in 1920, opened up new possibilities in the production of high-grade spar and has consequently played an important part in the rapid expansion of the fluorine chemical industry. Recently a heavy-mediums process has been developed, and this no doubt will contribute even more to the growth of this increasingly important industry. This development, known as the sink-float process, is adaptable to the upgrading of free-milling ores and also permits the recovery of a greater percentage of the calcium fluoride content of low-grade ores than was formerly possible.

*Economic Aspects.* World production of fluorspar is of the order of 1,100,000



TABLE I. U.S. Production and Imports of Fluorspar in 1949.

Shipped from U.S. mines		Imports	
State	Tons	Source	Tons
Illinois.....	120,881	Mexico.....	58,238
Kentucky.....	63,438	Newfoundland.....	15,344
Colorado.....	22,324	Spain.....	12,648
New Mexico.....	12,844	Italy.....	7,857
Utah.....	8,332	France.....	1,532
Nevada.....	5,847	<i>Total</i> .....	95,619
Others.....	3,038		
<i>Total</i> .....	236,704		

Source: reference (9).

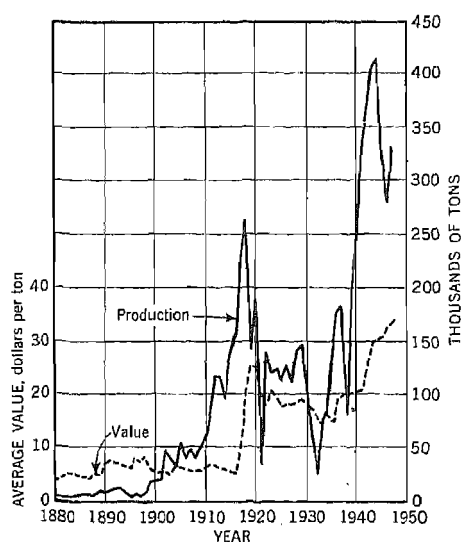


Fig. 1. Fluorspar shipped from U.S. mines, 1880-1947 (3).

short tons per year. Table I gives the 1949 figures for U.S. production and import of fluorspar, and Figure 1 shows the U.S. fluorspar production and its value from 1880 to 1947.

Fluorspar reserves in the United States, shown in Table II, have been estimated at about 9,000,000 tons of calcium fluoride as of January 1944 (4).

Deposits in Mexico and Newfoundland can supply both metallurgical- and acid-grade spar and, in addition, are geographically important. The deposits are extensive, but no estimate of reserves is available.

Large European reserves are found in Spain (5,000,000 tons), Germany (3,000,000 tons), and England (data not available). Russian deposits are believed to be extensive, but no information concerning them has been published.

**Grades.** Acid-grade spar may contain not less than 97%  $\text{CaF}_2$ , with the  $\text{SiO}_2$  constituting not more than 1.5%. Sulfides are highly objectionable. This grade is available as "No. 1 lump" or as the finely ground flotation product.

Ceramic grade spar must be pure white. It must contain not less than 95%  $\text{CaF}_2$  and not more than 3%  $\text{SiO}_2$ , 1%  $\text{CaCO}_3$ , and 0.12%  $\text{Fe}_2\text{O}_3$ . It must be substantially

TABLE II. Estimated U.S. Fluorspar Reserves.

Area	Crude ore, tons	$\text{CaF}_2$ , tons
Kentucky-Illinois.....	15,550,000	6,200,000
Rocky Mountain States.....	5,636,000	1,661,200
Southwestern States.....	2,111,000	810,500
Pacific Coast States.....	567,000	171,900
All other states.....	144,000	30,000
Alaska.....	308,000	128,900
<i>Total</i> .....	24,316,000	9,002,500

free of lead, zinc, and sulfur. The spar used for glass manufacture is about 55% through 100 mesh; a slightly finer material is used for enamels.

Metallurgical-grade spar is marketed as a product containing not less than 60 effective units of  $\text{CaF}_2$ , that is, the total fluorspar content less 2.5 times the silica content should be not less than 60%  $\text{CaF}_2$ . This grade is available as "gravel" or as "No. 2 lump." The gravel should pass a 1-in. screen and the amount of fines should not exceed 15%. No. 2 lump, which consists of pieces up to 5 or 6 in. in diameter, is sold for use as a flux in iron foundries for making high-grade castings.

Market quotations per ton (June 1950) for the various grades of fluorspar in bulk, carload lots at the mill, were: acid grade, \$43.50; ceramic grade, \$40.00; metallurgical grade, 70% effective  $\text{CaF}_2$  content, \$37.00, and 60% effective, \$34.00.

**Analysis.** Fluorspar is generally analyzed for total calcium, total fluorine, silica, carbonate, sulfide, and heavy metals. The mineral is decomposed with sulfuric acid, and calcium is estimated gravimetrically or volumetrically after precipitation as the oxalate. Fluorine is determined by the perchloric acid distillation method of Willard and Winter (10). Silica is determined by the method of Schrenk and Ode (8), which comprises determining the loss in weight after digestion with perchloric acid and evaporation with hydrofluoric acid. Carbonate is estimated by treatment of the ore with dilute acid in an alkalimeter, retaining the sulfide as the silver salt in the absorption bulbs.

**Uses.** Consumption of fluorspar in the United States during 1948 amounted to about 405,000 tons. Of this quantity about 55% was sold as metallurgical grade, about 15% as ceramic grade, and about 30% as acid grade. Figure 2 shows the consumption of fluorspar by industries in the U.S. from 1928 to 1948.

In metallurgy, fluorspar is used almost exclusively as a flux (see *Iron; Steel*). The basic open-hearth process, which consumed about 207,000 tons in 1948, uses fluorspar to increase the fluidity of the slag and to assist in the removal of certain impurities by volatilization. While the quantity of fluorspar varies, it has been estimated that, on an average, 5-6 lb. of spar is used in the production of each ton of steel. Electric-furnace steel required about 25,000 tons in the same year.

The chemical industry consumed more than 107,000 tons per year in 1948 for the

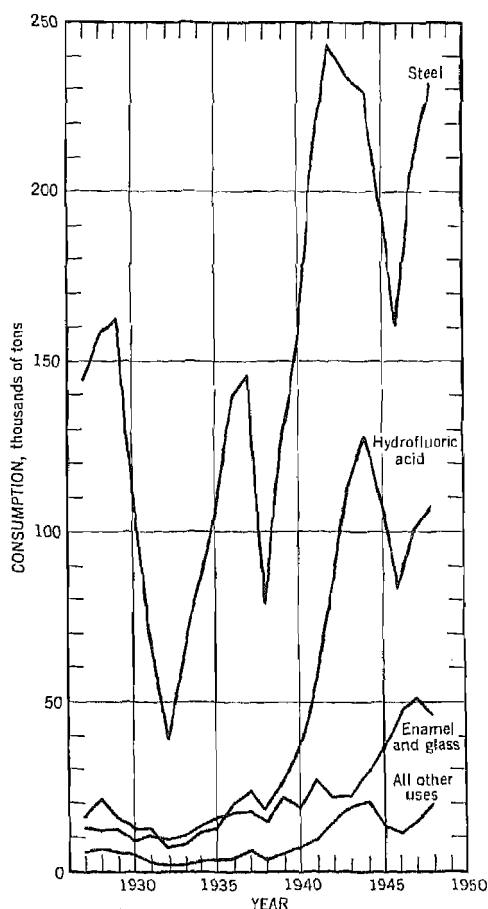


Fig. 2. U.S. consumption of fluorspar by industry.

manufacture of hydrofluoric acid (see "Hydrogen fluoride," p. 703). Hydrofluoric acid is the principal source of all other fluorine chemicals. The demand for fluorine compounds is growing so rapidly that it has been predicted that acid production will eventually displace the steel industry as the major outlet for fluorspar.

In 1948, the ceramic industry required 37,000 tons of fluorspar for the production of opalescent and opaque glass, which is used in the manufacture of bottles, jars, light bulbs, etc., and almost 9,000 tons for the production of vitreous enamels for coating iron and steel (see *Enamels; Glass*). In making the various types of opacified glass, from 5 to 50 pounds of fluorspar is used for every 100 pounds of sand.

Among the miscellaneous uses of fluorspar, which accounted for about 20,000 tons in 1948, are: iron-foundry operations, the manufacture of primary aluminum and primary magnesium, the production of welding-rod coatings and welding fluxes, and the manufacture of cement.

Colored varieties of fluorspar have found some use as an ornamental material, while very perfect clear crystals are used for optical purposes by virtue of their low index of refraction and relatively high transparency to infrared and ultraviolet radiation. Synthetic optical fluoride is available and, owing to its superior quality, is replacing natural crystal for most optical purposes.

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H. C. MILLER

**Chlorine Compounds.** See under "Halogen fluorides," p. 694.

### Chromium Trifluoride.

Chromium trifluoride (chromic fluoride),  $\text{CrF}_3$ , formula weight 109.01, is a green, monoclinic, crystalline salt; sp.gr. 3.78; slightly soluble in water and alcohol. Hydrates of the salt with 3, 4, 7, and 9 molecules of water of crystallization have been prepared. The trihydrate is the stable hydrate above 20°C.; the solubility, expressed as trihydrate, is 2.63% at 0°C. and 3.46% at 10°C. Chromium trifluoride is also reported to form a hydrate with  $3\frac{1}{2}$  molecules of water, known as the hemiheptahydrate. This salt loses water at 105°C. and reverts to the trihydrate.

The usual article of commerce is either a moist crystal or dried powder of indefinite composition as far as specific hydrates are concerned. It is characterized by the chromium content and water solubility rather than by the presence of any definite

hydrated salt. The hydrated salt is prepared by reducing chromium trioxide with organic reducing agents in the presence of a slight excess of hydrofluoric acid. The salt crystallizes out on cooling and is centrifuged and packed as a moist crystal.

Chromium trifluoride is used as a mordant in the dye industry, as in the Vigoureux printing of textiles. It has also been suggested as a preservative for wool.

G. C. WHITAKER

### Cobalt Compounds.

**Cobaltous fluoride**,  $\text{CoF}_2$ , formula weight 96.94, is a rose-colored granular powder; sp.gr. 4.46. It is prepared by heating cobaltous chloride in a stream of hydrogen fluoride gas, preferably in the presence of ammonium fluoride. The rose-red crystalline (monoclinic) dihydrate,  $\text{CoF}_2 \cdot 2\text{H}_2\text{O}$ , is produced by dissolving the oxide or carbonate of cobalt in aqueous hydrofluoric acid. The solubility of the anhydrous salt is given as 1.415 grams/100 ml. saturated solution at  $25^\circ\text{C}$ .

**Cobaltic fluoride** (cobalt trifluoride),  $\text{CoF}_3$ , formula weight 115.94, is a brown crystalline (hexagonal) material, sp.gr. 3.88, which is produced by heating cobaltous fluoride in a stream of fluorine at  $150$ – $200^\circ\text{C}$ . The trifluoride is hydrolyzed by water, but in the absence of moisture it is stable to relatively high temperatures, the partial pressure of fluorine being less than 0.1 atm. at  $600^\circ\text{C}$ . Cobalt trifluoride is one of the most common fluorine carriers used in the production of fluorocarbons.

F. D. LOOMIS

**Columbium Compounds.** See Vol. 4, p. 321.

### Copper Compounds.

**Cuprous fluoride**,  $\text{CuF}$ , formula weight 82.57, or  $\text{Cu}_2\text{F}_2$ , is a red crystalline powder; m.p.  $908^\circ\text{C}$ . It is formed by heating cupric fluoride in a stream of hydrogen fluoride at temperatures in excess of  $600^\circ\text{C}$ .; this reaction is complete only at  $1100$ – $1200^\circ\text{C}$ ., at which temperature the cuprous fluoride is appreciably volatile.

**Cupric fluoride**,  $\text{CuF}_2$ , formula weight 101.57, is a white crystalline solid; m.p.  $950^\circ\text{C}$ .; sp.gr. 4.23. Upon exposure to air, anhydrous cupric fluoride is converted to the blue monoclinic dihydrate,  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ . The latter compound is manufactured by dissolving the basic carbonate of copper in aqueous hydrofluoric acid. Cupric fluoride is soluble in water to the extent of 0.075 gram/100 ml. at  $25^\circ\text{C}$ .; it is also soluble in alcohol and acids. Cupric fluoride is formed when cupric oxide reacts with gaseous hydrogen fluoride at  $400^\circ\text{C}$ . Its uses as an opacifier in the manufacture of enamels, glass, and other ceramic ware, as well as in the preparation of brazing, soldering, and welding fluxes, have been reported.

F. D. LOOMIS

**Cryolite.** See under "Aluminum compounds," p. 672.

**Fluorspar.** See "Calcium fluoride," p. 689.

**Gallium Fluoride.** See *Gallium*.

**Germanium Compounds.** See *Germanium*.

**Halogen Fluorides.**

The halogen fluorides are binary compounds of chlorine, bromine, or iodine with fluorine. The development of practical means of producing fluorine on a large scale made their commercial production possible during World War II, as potential incendiary agents. Now chlorine trifluoride, bromine trifluoride, and bromine pentafluoride are available in steel containers. Uses are in the development stage and are based mostly on their reactivity, which approaches fluorine itself.

*Properties.* The best values now available for the physical properties of the halogen fluorides from a limited number of determinations are shown in Table I.

**TABLE I. Physical Properties of the Halogen Fluorides.**

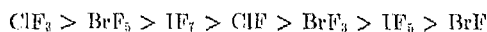
Property	IF <sub>5</sub>	IF <sub>7</sub>	BrF <sup>a</sup>	BrF <sub>3</sub>	BrF <sub>5</sub>	ClF	ClF <sub>3</sub>
State	Liquid	Gas	Gas	Liquid	Liquid	Gas	Gas
Color	Colorless	Colorless	Red	Colorless	Colorless	Colorless	Colorless
B.p., °C.	98	6	20	127	40.5	-100.8	11.3
F.p., °C.	9.6	4.5 (subl.)	-33	8.8	-61.3	-154	-83
Vapor pressure equation constants: <sup>b</sup>							
A	8.83	8.6604	—	8.41954	8.0716	15.738	7.42
B	2205	1602.6	—	2220.2	1627.7	3109	1292
C	0	0	—	0	0	153800	0
Liquid density equation constants: <sup>c</sup>							
A	4.38	—	—	3.623	3.496	—	2.729
B	0.004	—	—	0.00277	0.00346	—	0.00307

<sup>a</sup> Probably stable only at low temperatures.

<sup>b</sup> Vapor pressure:  $\log p = A - \frac{B}{T} + \frac{C}{T^2}$ , where  $p$  is given in mm. and  $T$  in °K.

<sup>c</sup> Density:  $d = A - BT$ , where  $d$  is given in grams/ml.

The most outstanding property of the halogen fluorides is their powerful oxidizing action on almost all matter, approaching fluorine itself in the case of chlorine trifluoride. Even argentous chloride and fluoride are converted to argentic fluoride, AgF<sub>2</sub>, by chlorine trifluoride. The estimated order of activity of the halogen fluorides is:



Except where a protective adherent film of fluoride is formed (as in mild steel, copper, and nickel), the halogen fluorides react with all metals, sometimes violently. Among the nonmetals, only the rare gases and oxygen and nitrogen fail to react. Even glass, asbestos, and cinders take fire in the halogen fluorides.

Organic compounds generally take fire in the halogen fluorides, giving products of undetermined composition.

*Preparation.* The halogen fluorides are made by direct reaction, usually of the elements in stoichiometric proportions. In most cases copper or nickel reactors are satisfactory. Iodine pentafluoride, IF<sub>5</sub>, is made from iodine and fluorine at room temperature, and iodine heptafluoride, IF<sub>7</sub>, can be made in 83% yield from iodine pentafluoride and fluorine at 250–270°C. Bromine monofluoride, BrF, can be made in low yield at 10°C. from bromine and fluorine with nitrogen as a diluent; bromine tri-

fluoride,  $\text{BrF}_3$ , is made from bromine and fluorine at  $15\text{--}50^\circ\text{C}$ ., and bromine pentafluoride,  $\text{BrF}_5$ , at  $200^\circ\text{C}$ . Chlorine trifluoride,  $\text{ClF}_3$ , is made from chlorine and fluorine at  $200^\circ\text{C}$ ., and chlorine monofluoride,  $\text{ClF}$ , can be made by mixing chlorine and chlorine trifluoride at room temperature.

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H. S. BOOTH AND J. T. PINKSTON

### Hydrogen Fluoride.

Hydrogen fluoride (hydrofluoric acid),  $\text{HF}$ , formula weight 20.008, the only binary compound of hydrogen and fluorine, was first obtained by Margraff in 1768. In 1771, it was prepared by Scheele by treating fluorspar (calcium fluoride) with concentrated sulfuric acid. This reaction remains the basis of all commercial production of hydrogen fluoride today.

Hydrogen fluoride is a colorless gas or liquid, which forms colorless solutions with water in all proportions. Liquid hydrogen fluoride, as well as its solutions down to approximately 70% hydrogen fluoride, fumes copiously; these fumes are very corrosive and dangerous to inhale. Solutions of lower acid content do not fume excessively. However, all hydrofluoric acid solutions must be handled with the greatest care, since contact with the skin will cause severe, slowly healing burns, and inhalation of the vapors may well cause death. Nevertheless, hydrogen fluoride is shipped and handled readily and safely in large amounts, the anhydrous acid and 60 and 70% aqueous solutions being shipped in tank-car quantities.

One property of hydrogen fluoride that attracted early interest was its rapid attack on glass, a reaction that produces gaseous silicon tetrafluoride, among other products. This led to the use of solutions containing hydrogen fluoride for etching and polishing glass. Today, large quantities of hydrogen fluoride are used in the production of fluorides, such as aluminum fluoride and synthetic cryolite (for the production of metallic aluminum), sodium fluoride (insecticidal use), sodium bifluoride (laundry products), a host of other metal fluorides, and numerous other inorganic fluorine compounds, such as the fluoroborates and fluosulfonic acid. The use of hydrogen fluoride in the preparation of metal fluorides (incident to the purification and subsequent production of the metal) is substantial, uranium and tantalum being representative metals in this class. The production of anhydrous hydrogen fluoride for use in the manufacture of aviation gasoline through hydrogen fluoride alkylation reached major proportions during World War II and, after a brief slump at the end of the war, again increased. Hydrogen fluoride is the source of the fluorine in substantially all organic fluorine compounds; where the hydrogen fluoride is not used directly under catalytic or electrochemical influence, as in the production of the Freon compounds and the fluorocarbons, it is the raw material for the manufacture of the elemental fluorine or metallic fluorides actually used.

Subsequent to the work of Scheele in 1771, in which hydrogen fluoride was definitely characterized, a pure and highly concentrated aqueous solution was prepared by Thénard and Gay-Lussac in 1809. Davy, starting in 1813, studied the electrolysis of hydrogen fluoride; Frémy, in 1856, first prepared anhydrous hydrogen fluoride by

heating dry purified potassium hydrogen fluoride; Gore, in 1869, studied the conductivity of pure hydrogen fluoride; and Moissan, in 1900, working with liquid of high purity, found that potassium fluoride would dissolve in anhydrous hydrogen fluoride to give a conducting solution, and prepared fluorine by the electrolysis of such a solution.

Dilute aqueous hydrofluoric acid was made in the U.S. before 1826. However, anhydrous hydrogen fluoride was first produced in commercial quantities in 1931, some 500 tons being produced by one manufacturer in that year and shipped by tank car for the manufacture of organic fluorides.

#### PHYSICAL AND CHEMICAL PROPERTIES

*Constants (7,8,9,15).* The physical properties of hydrogen fluoride do not differ regularly from those of the other hydrogen halides. This may be seen in the comparison of the series below, the abnormally high boiling point indicating a difference in constitution:

	HF	HCl	HBr	HI
M.p., °C.....	-83	-114	-87	-52
B.p., °C.....	+19.4	-85	-66	-36

The density of hydrogen fluoride in the gaseous state shows that its molecular weight is much greater than that corresponding to the simple formula, whereas the

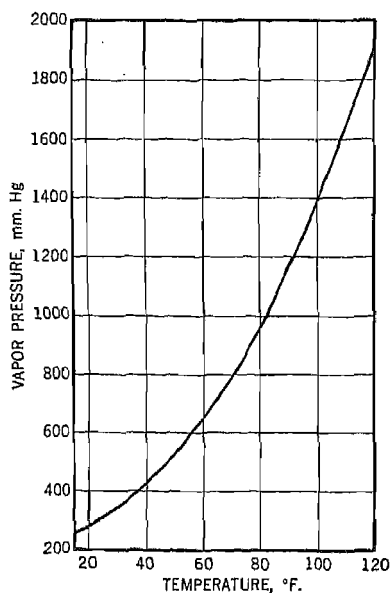


Fig. 1. Vapor pressure of anhydrous hydrogen fluoride (17).

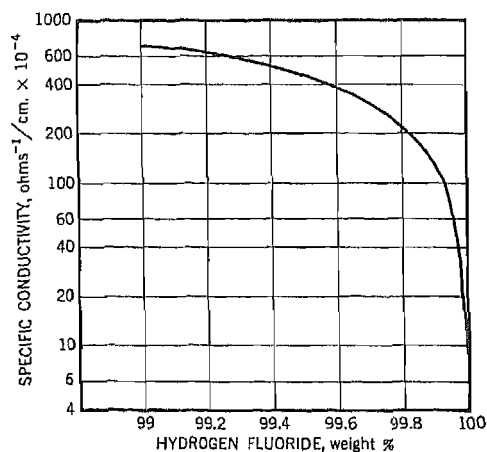


Fig. 2. Specific conductivity of hydrogen fluoride at 0°C. (4).

densities of the other halogen acids closely approximate the values corresponding to the unimolecular formulas. Hydrogen fluoride is therefore polymerized. In the liquid state as well, hydrogen fluoride is highly associated, probably as the hexamer. In the gaseous phase, polymers in the form of cyclics and open chains are said to exist in equilibrium with hydrogen fluoride molecules; this equilibrium shifts with tem-

perature and pressure. For gaseous hydrogen fluoride in equilibrium with the liquid, the apparent molecular weight is about 86 at  $-35^{\circ}\text{C}.$  and about 67 at  $10^{\circ}\text{C}.$  (3,19). There is associated with this polymerization a considerable heat effect; thus, there is an abnormal heat change with variation of pressure at constant temperature. There is also an abnormally high apparent heat capacity of the gas, which is due to the depolymerization of the gas with rising temperature at constant pressure. The following physical data have been reported for anhydrous hydrogen fluoride: vapor pressure, see Figure 1; sp.gr. at  $t^{\circ}\text{C}.$ ,  $1.0020 + 0.002265t + 0.000003125t^2$ ; sp.heat,  $C_p$ , 0.348 cal./gram for gas at  $25^{\circ}\text{C}.$ , 0.81 for liquid at  $-10^{\circ}\text{C}.$ , and 0.85 for liquid at  $0^{\circ}\text{C}.$ ; crit.

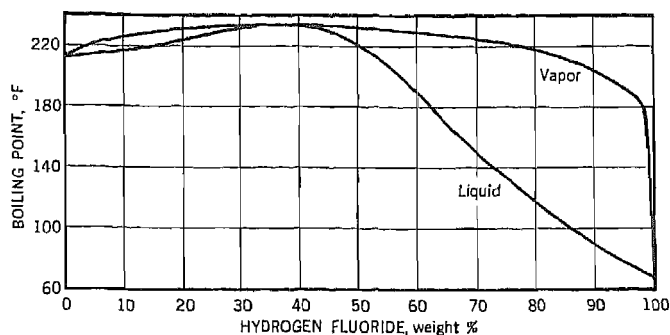


Fig. 3. Aqueous hydrogen fluoride—liquid-vapor equilibrium at the boiling point (12).

temp.,  $230.2^{\circ}\text{C}.$ ; crit. pressure, 94.5 atm.; heat of formation, 71.0 kg.-cal./20 grams (20 is the formula weight of HF) for liquid at  $18^{\circ}\text{C}.$ , and 64.45 kg.-cal./20 grams for gas at  $100^{\circ}\text{C}.$ ; heat of fusion at  $-83^{\circ}\text{C}.$ , 1094 cal./20 grams; heat of vaporization at  $19.4^{\circ}\text{C}.$ , 97.5 cal./gram; heat of dissociation  $((\text{HF})_6 \rightarrow 6 \text{ HF})$ , 40.8 kg.-cal./120 grams; heat of solution, 4.56 kg.-cal./20 grams for liquid at  $17^{\circ}\text{C}.$  in 400 moles of water, and 11.56 kg.-cal./20 grams for gas at  $25^{\circ}\text{C}.$  in 400 moles of water; viscosity at  $0^{\circ}\text{C}.$ , 0.53 centipoise; surface tension at  $0^{\circ}\text{C}.$ , 10.2 dynes/cm.; dielectric constant at  $0^{\circ}\text{C}.$ , 83.6; specific electrical conductivity,  $4 \times 10^{-4}$  ohm $^{-1}$ /cm. (see Fig. 2); solubility at  $5^{\circ}\text{C}.$

TABLE I. Properties of Aqueous Solutions of Hydrogen Fluoride.

HF, % by wt.	F.p., $^{\circ}\text{F}.$	Heat of soln., B.t.u./lb. HF	$d_4^{25}$	Sp.heat <sup>a</sup> at $80^{\circ}\text{F}.$	Vapor pressure of HF at $80^{\circ}\text{F}.$ , mm. Hg	Viscosity at $32^{\circ}\text{F}.$ , centipoises
10	+12	464	1.040	0.92 <sub>7</sub>	< 1	1.68
20	-23	454	1.080	0.86 <sub>2</sub>	< 1	1.57
30	-95	439	1.119	0.81 <sub>0</sub>	1.8	1.46
40	-55	415	1.159	0.76 <sub>8</sub>	9.9	1.34
50	-33	380	1.198	0.74 <sub>0</sub>	37	1.21
60	-42	332	1.235	0.73 <sub>9</sub>	97	1.05
70	-95	272	1.258	0.75 <sub>0</sub>	200	0.85
75	-109	238	1.262	0.76 <sub>0</sub>	—	0.76
80	-149	198	1.259	0.77 <sub>2</sub>	365	0.68
85	-151	155	1.240	—	—	0.61
90	-162	108	1.178	—	640	0.54
95	-134	56	1.089	—	—	0.49

<sup>a</sup> Third significant figure uncertain.

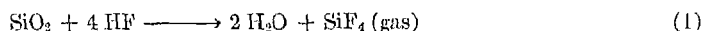


(in % by weight), 2.54 in benzene, 1.80 in toluene, 1.12 in *m*-xylene, and 0.27 in tetralin.

It is interesting to note that, like the other hydrogen halides, hydrogen fluoride forms a constant-boiling mixture with water; this mixture has a composition of 38.2% by weight of HF and a boiling point of 112.2°C. Other physical data on aqueous hydrofluoric acid are summarized in Table I (8) and Figure 3.

*Reactions (9).* The chemical properties of hydrogen fluoride are generally similar to those of the other hydrogen halides in that aqueous hydrogen fluoride undergoes normal acid reactions with metals above hydrogen in the e.m.f. series, as well as with metal oxides, hydroxides, and carbonates to form salts. While hydrogen fluoride is an extremely reactive compound, it is actually a rather weak acid. In aqueous solution it is comparable to acetic acid, having an ionization constant of about  $7.4 \times 10^{-4}$ . Aqueous solutions of the alkali fluorides are strongly alkaline because of hydrolysis.

Hydrofluoric acid is distinguished from all other acids by its ability to dissolve silica and silicic acid, a reaction that is utilized technically for etching glass, and in the laboratory for detecting fluorine or silicic acid as well as for decomposing silicates. The reaction may be represented as follows:



The velocity of this reaction depends upon the nature and fineness of the siliceous material as well as upon the temperature. Also unusual among the reactions of hydrogen fluoride is its attack on boron trioxide to form hydroxyfluoboric and fluoboric acids.

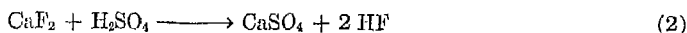
The ability of hydrogen fluoride to form stable complexes with metal fluorides, such as  $\text{AgF} \cdot \text{HF}$ ,  $\text{KF} \cdot \text{HF}$ ,  $\text{KF} \cdot 2\text{HF}$ ,  $\text{NaF} \cdot \text{HF}$ , and  $\text{NH}_4\text{F} \cdot \text{HF}$ , is characteristic. Hydrogen fluoride forms three hydrates, which separate as the solid phases when aqueous solutions, as follows, are cooled below their respective freezing points:

Concn. range, mole fraction of HF	Freezing range, °K.	Hydrate (solid phase)
0.276–0.685	202.9–197.9	$\text{H}_2\text{O} \cdot \text{HF}$
0.685–0.776	197.9–171.7	$\text{H}_2\text{O} \cdot 2\text{HF}$
0.776–0.883	171.7–162.2	$\text{H}_2\text{O} \cdot 4\text{HF}$

Hydrogen fluoride is a very active dehydrating agent. It does not, however, dehydrate primary alcohols at ordinary temperatures, nor does it dehydrate acetone as rapidly as sulfuric acid does at the same temperature.

#### MANUFACTURE

While many methods for the manufacture of hydrogen fluoride have been proposed (of which a great number have involved the recovery of hydrogen fluoride from the silica fluorides or fluosilicic acid produced from the den gases generated in phosphate rock acidulation), practically all commercial hydrogen fluoride production has been based upon the reaction of fluorspar and sulfuric acid:



Fluorspar (fluorite), the most important source of fluorine today, is calcium fluoride, which in pure form consists of 48.7% fluorine and 51.3% calcium (see p. 689). Fluorspar usually occurs in a gangue of varying quantities of limestone, calcite, and quartz with minor amounts of sphalerite, galena, pyrite, and chalcopyrite. Since as

pure a fluorspar as possible is desired for hydrogen fluoride manufacture, the separation of these impurities is most important. Acid-grade fluorspar is the purest grade produced. Before 1935, acid-grade fluorspar consumption did not exceed 20,000 tons per year and amounted to less than 10% of total fluorspar consumption. During this period, lump spar exceeding 98%  $\text{CaF}_2$  and containing less than 0.5%  $\text{SiO}_2$  was readily available. However, after 1935, the rapidly increasing demand for acid-grade spar (amounting to 129,000 tons in 1944, or 31% of all fluorspar consumed), as well as for other grades, made imperative the beneficiation of fluorspar ores and particularly the use of flotation processes for the production of acid-grade spar.

Commercial acid-grade fluorspar is a finely ground flotation product having the following typical screen analysis: 1% on 100 mesh, 12% on 200 mesh, 30% on 250 mesh, 12% on 325 mesh, and 45% through 325 mesh. It contains 97.5–98%  $\text{CaF}_2$ , 1.0% max.  $\text{SiO}_2$ , and 0.05% max. S, with  $\text{CaCO}_3$  the principal remaining component.

The ability of the reaction (eq. 2) to proceed to the maximum degree in commercial operation is influenced by the fineness of the fluorspar, the concentration of the sulfuric acid used, the ratio of sulfuric acid to fluorspar, the temperature of the reaction, the time allowed for completion of the reaction, and the intimacy of mixing of the acid and spar.

In general, with other conditions constant, the finer the fluorspar the readier is the liberation of fluorine values from the spar and, thus, the better are the yields. Fluorspar of the screen size indicated above has been commercially utilized directly in the hydrogen fluoride kilns with good yields. However, it has been the practice of some manufacturers to grind this material further. Such additional grinding is an expensive operation involving some small handling loss of fluorspar, and a decision to employ this procedure must be based upon an economic evaluation of the improved yields as compared with other means of securing the same results.

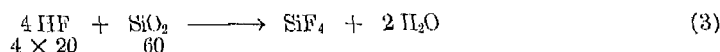
Sulfuric acid with a concentration as low as 93% or as high as 98% has been reported to be used in hydrogen fluoride manufacture. The more dilute the acid (in this range), the more fluid is the reacting mass during initial mixing, and the greater is the ease with which the liberation of the fluorine values from the fluorspar takes place. Two important factors offset this: (1) the more dilute sulfuric acid is much more corrosive to the hydrogen fluoride generator, and (2) the greater amount of water present will leave the generator with the hydrogen fluoride gas and may be undesirable. Thus, modern practice has established 96% sulfuric acid as the minimum desirable acid strength. The use of sulfuric acid stronger than 98% will reduce the amount of water introduced into the generator and may be less corrosive to the materials of construction; however, the vapor pressure of sulfuric acid, which increases rapidly with concentration above 98%, will be such that excessive amounts of sulfuric acid will leave the generator with the hydrogen fluoride gas, thereby not only reducing the quantity available for reaction with spar but also contaminating all or part, depending on the recovery system, of the hydrogen fluoride produced. In addition, the formation of fluosulfonic acid, which also has an appreciable vapor pressure, will be increased and thus tend to deplete the reacting mass of sulfuric acid and contaminate the product.

The ratio of sulfuric acid to fluorspar charged to the hydrogen fluoride generator is seldom the exact stoichiometric ratio, since, depending upon the relative cost of fluorspar and sulfuric acid, one or the other is used in slight excess. In U.S. practice, with fluorspar costing approximately  $3\frac{1}{2}$  times as much as sulfuric acid, economic operation demands the maximum release of fluorine from fluorspar and justifies the use of a 5–

10% excess of sulfuric acid. It should be recognized, however, that too great an excess of sulfuric acid will result in a "wet" residue calcium sulfate, which will tend to be strongly fuming unless the sulfuric acid is driven out of the generator with the hydrogen fluoride by high generator temperatures.

The reaction of calcium fluoride and sulfuric acid is endothermic, and thus heat must be supplied to complete the reaction in a reasonable period of time. To effect a release of over 98% of the fluorine in the fluorspar, the reaction time is normally 30-60 minutes at 200-250°C., with the hydrogen fluoride leaving the generator at 100-150°C. Obviously, the lowest operating temperatures at which good yields are obtainable are desirable to minimize corrosion of the generator.

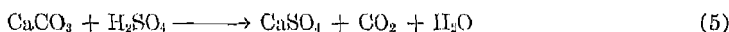
In addition to the main reaction, several others take place in the generator. Of these, the most significant involves the silica content of the fluorspar:



Since this reaction is substantially stoichiometrically complete,  $1\frac{1}{3}$  parts by weight of hydrogen fluoride is consumed per part of silica in the fluorspar. This reaction represents a loss of hydrogen fluoride, since the silicon tetrafluoride is of little value as compared to hydrogen fluoride. Furthermore, if the hydrogen fluoride is recovered as an aqueous solution, a further loss of hydrogen fluoride is occasioned by the reaction:



The reaction of calcium carbonate in the generator results in a nonproductive consumption of sulfuric acid:



This yields a gas that dilutes the hydrogen fluoride leaving the generator, and may cause difficulty because of excessive foaming in the generator.

Reactions arising from the sulfur content of the fluorspar cause the undesirable presence of hydrogen sulfide or sulfur dioxide in the product acid. A further result may be the deposition of elemental sulfur in the gas lines from the generator, eventually causing plugging of the lines.

The earliest equipment for generating hydrogen fluoride was simply a lead pot or retort, in which a mixture of sulfuric acid and fluorspar was heated until the bulk of the hydrogen fluoride was driven off as a gas and absorbed as a weak water solution in lead pans. The retort was then opened and the calcium sulfate cake broken up and removed before charging the next batch.

The mechanical development of the generating equipment has followed normal and logical steps. Agitators were added to keep the calcium sulfate in a granular form for more complete liberation of the hydrogen fluoride and to permit greater facility in emptying the generator. Cast iron and steel were used for generator construction to permit the use of higher temperatures. Generators were made larger to give greater production. Semicontinuous generators were then built; in these, a surging evolution of gas was experienced as fresh batches of fluorspar and acid were added to the already reacting mixture. The residual calcium sulfate was removed intermittently.

This development has culminated in two types of generators commonly used today. Both are fed with fluorspar and acid continuously and automatically, and the hydrogen fluoride is generated and removed continuously, as is the calcium sulfate residue.

The first type consists of a long stationary reactor having a U-shaped cross section and containing a central shaft, extending the full length, equipped with mixing and conveying paddles. The spar and acid are fed continuously through the cover at one end, the reacting mass being mixed and conveyed to the opposite end, where it is discharged by means of a screw conveyor or other gas-seal mechanism. The reactor is enclosed in a refractory setting, which permits the application of heat by circulating products of combustion. A pressure of 1–2 in. of water is maintained in the reactor to prevent the admixture of air with the hydrogen fluoride, which customarily leaves through the cover by means of a steel pipe. The hydrogen fluoride exit may be located at any point along the reactor, but is preferably placed near the feed end and thus at the point of maximum reaction. The reactor is constructed of cast iron or steel, while the mixer paddles are of high chrome–nickel alloy, such as Alloy 20. These reactors are built in lengths up to 60 ft. or more and have a capacity of 500–1000 lb. of fluorspar per hour.

The second type of reactor consists of a horizontal steel cylindrical vessel rotating on trunnions at 3–5 r.p.m., much the same as a rotary dryer. The diameter may be up to 6 ft., while the length usually does not exceed 40 ft. Kilns of this type operated by I. G. Farbenindustrie were 46 in. I.D. by 30 ft. long and had a capacity of approximately 2000 lb. of spar per hour. The steel shell and end plates were approximately  $1\frac{1}{8}$  in. thick; a replaceable steel inner lining, approximately  $\frac{3}{4}$  in. thick, was also used. Spar was fed by an axial screw conveyor at one end, the sulfuric acid being added continuously through the hollow spar-conveyor shaft. The residue and hydrogen fluoride were discharged axially at the opposite end into a stationary hood provided with mechanical seals to prevent entrance of air into the reactor. The hydrogen fluoride left through a steel pipe at the top of this hood, and the calcium sulfate residue was discharged by means of a heavy screw conveyor to a water slurry tank from which it was pumped to waste. All but the driving gear and riding rings was enclosed in a refractory-lined housing. The reactor was externally gas-fired, burners being distributed along the length of the kiln. Such units have a capacity of 8–10 tons per day of 100% hydrogen fluoride and are generally similar to reactors of this type used in U.S. practice.

The recovery of hydrogen fluoride from the gases leaving the reactor has also developed from batch to continuous operation and from the collection of the hydrogen fluoride as a weak aqueous solution to its recovery as a strong aqueous solution or as anhydrous hydrogen fluoride.

Since hydrogen fluoride is readily soluble in water and exerts a low vapor pressure over dilute solutions, early recovery systems consisted simply of covered shallow lead trays containing water or weak acid solutions, in which the gases were absorbed as they passed across the surface. Later, various designs of absorbing towers, usually of lead construction, were utilized. The gases to be absorbed passed successively through two or more towers, a lead-covered fan being used to overcome the resistance to flow. Each tower was provided with a rundown tank, in which the acid was cooled and from which it was recirculated through the tower. Water was fed to the last tower of the series. The accumulation of acid at each rundown tank overflowed to the tower preceding. The strongest acid, from the first tower, was normally maintained at 60% hydrogen fluoride, the highest customary shipping strength at the time. Circulation of acid solutions over the towers was effected by means of air lifts or pumps made of lead, hard rubber, or carbon.

With the advent of demands for anhydrous hydrogen fluoride, systems combining absorption and condensation were devised, and equipment for handling acid containing 60% or more hydrogen fluoride was fabricated of steel. With the use of condensation procedures, it became increasingly necessary to avoid or minimize the presence of air in the hydrogen fluoride gas, and reactors were designed accordingly. Similarly, since appreciable amounts of sulfuric acid, silicon tetrafluoride, and water vapor are present in the hydrogen fluoride gas leaving the generator, procedures to remove these impurities became necessary to meet anhydrous hydrogen fluoride specifications. The process of J. C. Lawrence (22) is typical of those that developed as a result of these changing requirements. In this process, hydrogen fluoride gas from a mechanically agitated type of reactor is passed through a packed tower to separate as much of the sulfuric acid present in the gas stream as possible. The gas is then cooled and partially condensed in a trombone type of cooler externally sprayed with water. The condensate from this unit consists of 60-80% hydrogen fluoride, and 2-5% sulfuric acid; the balance is essentially water, although some fluosilicic acid is usually present. The temperature of this condensation step is such that the exit gas is essentially anhydrous hydrogen fluoride, which is recovered by cooling and condensing at  $-20^{\circ}\text{C}$ . The vent gas from the low-temperature condenser is essentially silicon tetrafluoride and hydrogen fluoride, the latter usually being present in amounts that approximate the stoichiometric requirements for fluosilicic acid when the vent is absorbed in water in a packed tower. The acid collected in the trombone cooler-condenser may be distilled in a packed or conventional tray tower of copper construction. It will, with proper control of temperature, yield anhydrous hydrogen fluoride as an overhead product and a bottom of any desired strength down to about 38% by weight of hydrogen fluoride.

Another practice has been the use of a series of steel vertical shell-and-tube condensers followed by final hard-rubber-lined water absorbers to pick up the last of the hydrogen fluoride. Thus, in one plant, the gas leaving the generator at  $130^{\circ}\text{C}$ . dropped to  $100^{\circ}\text{C}$ . in the gas ducts and was cooled to  $80^{\circ}\text{C}$ . in a vertical shell-and-tube cooler. Very little hydrogen fluoride condensed in this unit, but dust and some sulfuric acid did separate out. The gas was then cooled further to  $30^{\circ}\text{C}$ . in a second vertical shell-and-tube condenser, in which 60-65% of the hydrogen fluoride was recovered as 75-86% acid containing 1-3% fluosilicic acid and 1-4% sulfuric acid. The gas was still further cooled to  $-10^{\circ}\text{C}$ . in a similar condenser, and 10-15% of the hydrogen fluoride was recovered as 96-98% acid containing 0.1% sulfuric acid and little or no fluosilicic acid. The remaining 20-25% of hydrogen fluoride was recovered as a 40% acid containing 6-10% fluosilicic acid and no sulfuric acid. The acid from the first two condensers may be combined and distilled to yield anhydrous hydrogen fluoride.

Generalizations regarding materials of construction where hydrogen fluoride and its aqueous solutions are to be handled have proved in numerous instances to be quite misleading, and laboratory corrosion tests must be looked upon only as the most general guides. In spite of these facts, readily available materials have been found to meet each specific problem encountered. The presence of impurities such as sulfur compounds and fluosilicic acid, and the degree of aeration, velocity, and temperature are important considerations. In the manufacture of hydrogen fluoride, steel generators have long been used satisfactorily, and lines and other equipment handling the gases from the generator may be of steel so long as acid condensing from these gases contains not less than 70% hydrogen fluoride. Weaker acids must be handled in non-ferrous materials such as carbon, lead, bronze, or Monel. Lead is sensitive to the

presence of fluosilicic acid and cannot be used when more than 2-3% of that acid is present. Monel is adversely affected by aeration and the presence of sulfur compounds. Natural rubber and neoprene are useful for strengths below 60% hydrofluoric acid, and particularly below 40%. Copper has been widely used for the distillation of hydrofluoric acid solutions to produce anhydrous hydrogen fluoride. Steel valves with Monel trim are generally satisfactory for anhydrous hydrogen fluoride, and bronze valves with Monel trim are suitable for aqueous hydrofluoric acid. While a wide variety of materials have had limited use for gaskets, Teflon has proved to be most satisfactory, and pump and valve packings of Teflon have given excellent performance.

The raw material, labor, and energy requirements for the production of hydrogen fluoride are given in Table II.

TABLE II. Requirements for Hydrogen Fluoride Manufacture.

Yield, based on $\text{CaF}_2$ .....	85-90%
Yield, based on $\text{H}_2\text{SO}_4$ .....	75-85%
Operating labor.....	10-15 man-hours/ton
Repair labor.....	10-15 man-hours/ton
Electricity.....	700 kw.-hr./ton
Fuel.....	7,000,000 B.t.u./ton
Water.....	9,000 cu.ft./ton

## ECONOMIC ASPECTS

Of the fluorine-containing minerals, only three, cryolite, fluorapatite, and fluorspar, are of commercial significance. Cryolite,  $\text{Na}_3\text{AlF}_6$ , has the highest fluorine content of any known commercial mineral, 54% by weight. It is mined only at Ivigtut, Greenland and, because of its cost, is not used as a raw material for the fluorine chemical industry (see "Cryolite," p. 672).

Fluorapatite or rock phosphate,  $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ , which has a fluorine content of about 3.7% by weight, is a very common mineral quite widely distributed throughout the world (see *Fertilizers*). However, as the fluorine from the rock-phosphate industry is recovered as fluosilicic acid, which is not conveniently convertible to hydrogen fluoride by known processes, fluorapatite has entered the fluorine chemical field only as a source of fluosilicic acid and the fluosilicates (see "Silicon tetrafluoride," p. 722; "Fluosilicic acid," p. 725). It has been pointed out by others that the phosphate rock reserves in the U.S. alone are equivalent in fluorine content to the world's fluorspar requirements for approximately 600 years at present levels. Thus, an inexpensive means of converting fluosilicic acid to hydrogen fluoride would mean a tremendous conservation of the more limited fluorspar reserves.

The most important fluorine-containing mineral in industry is fluorspar or fluorite (5), which contains 48.7% by weight of fluorine (see also "Calcium fluoride," p. 689). Of the three principal commercial uses of fluorspar (metallurgical, ceramic, and chemical), the chemical industry has since 1936 established itself as the second largest consumer of spar, increasing the demand from 20,000 tons in 1936 to 129,000 tons in 1944. The annual consumption of acid-grade fluorspar since 1927 is shown on p. 691, which portrays most vividly the rapid expansion of the fluorine chemical industry since 1938 to a peak production in 1944. While there was a marked falling off of production of hydrogen fluoride in 1945 and 1946 as a result of relaxation of war demands, all indications, based upon the tremendous research and development effort devoted to

fluorine chemicals, are that the uptrend, which was evident in 1947 and 1948, will continue.

Actual production figures for hydrogen fluoride are incomplete and not too informative. However, since the ratio of fluorspar consumed to hydrogen fluoride produced is reasonably well fixed, the application of a conservative ratio (2.4 tons of fluorspar to 1.0 ton of 100% hydrogen fluoride) to the U.S. Bureau of Mines fluorspar consumption data gives reasonably reliable total-production data. These figures, of course, include all aqueous and anhydrous hydrogen fluoride whether consumed at the manufacturers' works or sold to others; it also includes that which is consumed in the production of synthetic cryolite and aluminum fluoride by the aluminum industry. Table III shows the total U.S. hydrogen fluoride production as estimated by using this factor.

TABLE III. Estimated U.S. Production of Hydrogen Fluoride.

Year	Acid-spar consumption, tons	HF (100%) production, tons	Year	Acid-spar consumption, tons	HF (100%) production, tons
1936	20,100	8,400	1942	81,600	34,000
1937	24,100	10,000	1943	113,614	47,300
1938	18,900	7,900	1944	120,553	53,700
1939	26,300	11,000	1945	100,315	45,400
1940	37,000	15,400	1946	83,901	35,000
1941	56,000	23,400	1947	100,363	41,800

The market price for anhydrous hydrogen fluoride has remained quite stable for a number of years, varying between 16.0 and 16.5¢/lb. in tank-car quantities.

#### SPECIFICATIONS AND STANDARDS

Hydrogen fluoride and its aqueous solutions are marketed in a wide variety of concentrations including 30%, 48%, 52%, 60%, 70%, and anhydrous. Acid containing less than 60% HF is shipped in 13-gal. rubber drums conforming to I.C.C. Spec. 43A, and carrying a corrosive-liquid, white label (9a). These acids usually contain small amounts of fluosilicic and sulfuric acids as impurities, together with 0.01-0.02% of metals (iron), although acid extremely low in all impurities is available. All the commercial grades of hydrofluoric acid are colorless liquids and the concentrations containing less than 60% hydrogen fluoride are nonfuming.

Hydrofluoric acid of 60 and 70% concentration may be shipped in 20-, 55-, and 110-gal. steel drums meeting I.C.C. Container Regulation 5A, and carrying corrosive-liquid, white labels, and in steel tank cars containing approximately 30 tons of acid and conforming to I.C.C. Regulation 103A. Again, the usual impurities are fluosilicic and sulfuric acids with a small amount of iron. Commercial acid of 70% strength is available with as little as 0.1% each of sulfuric and fluosilicic acids.

Anhydrous hydrogen fluoride, while relatively a newcomer to the ranks of tonnage chemicals, has rapidly become one of the purest, if not the purest, available. This has been brought about primarily by the fact that in each of the various fields into which it moves, one or more of the normal impurities is deleterious to efficient operation. The result has been that, while commercial anhydrous hydrogen fluoride contains a minimum of 99.5% HF, commercial shipments have been made wherein a guarantee of 99.9% HF was held. In Table IV representative analyses are given.

TABLE IV. Analysis of Commercial Anhydrous Hydrogen Fluoride.

Component	High-purity	Regular
HF, %.....	99.9.....	99.5
H <sub>2</sub> SiF <sub>6</sub> , %.....	0.02.....	0.08
SO <sub>2</sub> , %.....	0.02.....	0.18
II <sub>2</sub> SO <sub>4</sub> , %.....	0.005.....	0.05
H <sub>2</sub> O, %.....	0.02.....	0.2

Anhydrous hydrogen fluoride is shipped in steel cylinders, I.C.C. Spec. 4B, not brazed (or other cylinders of superior specification, such as I.C.C. 3A 480) and in insulated forged-steel tank cars, I.C.C. Spec. 105A 300, containing approximately 23,000, 43,000, or 83,000 lb. of hydrogen fluoride. Although under I.C.C. regulations it is classed as a "corrosive liquid," it is shipped in compressed-gas containers primarily because of its extremely hazardous nature. All the precautions usually observed in handling compressed gases should be exercised, and full recognition of the dangerous nature of the fumes and liquid acid must be taken. Complete information on the handling and discharge of containers for anhydrous and aqueous hydrofluoric acid is given in Manufacturing Chemists' Association Manuals (10).

#### HEALTH AND SAFETY FACTORS

Years of experience in the manufacture of hydrofluoric acid have shown that this material can be handled with relative safety, providing the hazards are recognized and necessary precautions taken. Hydrofluoric acid is extremely corrosive to the skin and, depending on the strength of acid and length of contact, skin changes range from minor burns to serious ulcers, which heal very slowly. To avoid the severe penetration and delayed attack characteristic of acid fluorides, the skin or eyes should be flushed with copious amounts of water and then given immediate medical attention. Inhalation of the vapors may cause fatal edema of the lungs (20) and, although experience has shown that the fatal vapor concentration for a man in good health is so irritating to the eye and upper respiratory tract that a lethal dose could be received only during unconsciousness or by the sudden inhalation of a spray, it is inadvisable to place full reliance on this warning. When working with hydrofluoric acid, the proper use of protective clothing, goggles, face shields, etc., is important, and a full knowledge of approved methods of first aid is mandatory. Reference should be made to the instructions published by Manufacturing Chemists' Association (10), as well as those in other publications (11,13).

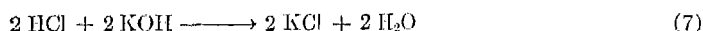
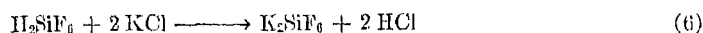
#### ANALYSIS

The analysis of hydrogen fluoride and its aqueous solutions (14), in so far as its manufacture is concerned, consists essentially in the determination of hydrogen fluoride and of the commonly associated impurities: silicon tetrafluoride or fluosilicic acid, sulfuric acid and fluosulfonic acid, sulfur dioxide, water, and metals (chiefly iron). For manufacturing control, analyses of fluorspar for moisture, calcium carbonate, silica, and calcium fluoride, and of reactor residues for calcium fluoride, hydrogen fluoride, and sulfuric acid content, are required.

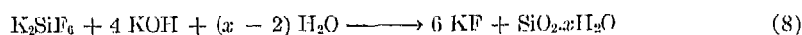
In the analysis of aqueous solutions to determine fluosilicic acid, advantage is taken of the extremely low solubility in 50% alcohol of potassium fluosilicate, which



does not hydrolyze below 10°C. A cold titration, to a phenolphthalein end point, of a solution containing hydrogen fluoride, fluosilicic acid, and sulfuric acid, to which potassium chloride and alcohol have been added, will give a figure corresponding to all of the hydrogen fluoride and sulfuric acid and one-third of the fluorine in the fluosilicic acid:



The solution that has been titrated cold may then be heated to 30°C. and titrated to a permanent end point, this final hot titration giving two-thirds of the fluorine in the fluosilicates:



Sulfuric acid, as well as fluosulfonic acid if present, is determined by titration after repeated evaporations to eliminate hydrogen fluoride.

Samples of anhydrous hydrogen fluoride are most conveniently collected for the laboratory in small (about 4 lb.) evacuated steel cylinders. It should be remembered that a cylinder must never be filled to more than 85% of its water capacity.

The technique of dilution of the anhydrous hydrogen fluoride for analytical purposes is most important because of the heat evolved, the volatility of the hydrogen fluoride, and possible hazards to the operator. The preferred method (14,21) involves the dilution of the sample with ice at the bottom of a cylindrical hard-rubber pipe in the upper section of which, supported on a grid, is additional ice to absorb and cool such vapors as are formed during dilution in the lower section. Sulfur dioxide, sulfuric acid, fluosilicic acid, total acidity, and hydrogen fluoride (by difference from total acidity) are all determined on the diluted sample. The water content of the acid may be determined directly by use of a conductivity cell, the acid being cooled to 15°C. Correction should be made for sulfuric acid, if present in appreciable amounts. An alternate method for the determination of fluosilicic acid in anhydrous hydrogen fluoride (1) involves the conversion of fluosilicic acid to silicomolybdic acid, which is determined photometrically.

## USES

Hydrofluoric acid is the "key chemical" in almost all fluorinating processes (2,7,16). It also finds extensive application in nonfluorinating processes as a catalyst and reaction medium (18). An evaluation of the relative economic importance of any one of the many uses of hydrogen fluoride would be almost impossible.

The aluminum industry is one of the heaviest consumers of fluorine compounds. Cryolite comprises the molten bath in the electrolytic cells, and aluminum fluoride and fluorspar in small amounts are added directly while the cells are operating. Synthetic cryolite is prepared, in general, by the reaction of hydrofluoric acid with sodium aluminate solutions. Aluminum fluoride is prepared by the reaction of alumina hydrate and hydrofluoric acid. It is difficult to arrive at exact consumption figures, but the magnitude may be approximated. It has been reported (5) that 0.1 lb. of cryolite is required for each pound of aluminum produced. On this basis, 60,000 tons of cryolite was required in 1947 to produce 600,000 tons of aluminum. From a consideration of the natural cryolite imports, if a maximum of 20,000 tons from this source is assumed,

there was produced at least 40,000 tons of synthetic cryolite in 1947, requiring approximately 23,000 tons of hydrogen fluoride.

A second major use of hydrogen fluoride (anhydrous) had its inception in 1930 when Midgley and Henne announced the commercial production of a new group of refrigerants, the Freon compounds (see "Fluorinated hydrocarbons" under *Fluorine compounds, organic*). In general, they are made by the fluorination of a polychlorinated methane or ethane by antimony trifluoride in the presence of a catalyst, usually antimony pentachloride. Anhydrous hydrogen fluoride, which is fed to the reactor with the material to be fluorinated, continuously regenerates the active fluorinating agent, antimony trifluoride. With a proposed production capacity of over 28,000 tons per year as reported in 1944, the Freon compounds are by far the most important organic fluorides, and at this rate would require approximately 9,000 tons per year of hydrogen fluoride.

A large demand for anhydrous hydrogen fluoride was created during World War II as the result of the development of the hydrogen fluoride-alkylation process by the petroleum industry (2,6,7). Here hydrogen fluoride is used as a catalyst for the conversion of olefins and isoparaffins, for example, butylene and isobutane, into an "alkylate" consisting of mixtures of isomers of heptane, octane, etc. (see *Alkylation; Petroleum*). The alkylate has an A.S.T.M. octane rating of about 93, and is widely used in high-octane aviation blends. Hydrogen fluoride allocations for this purpose in 1944-45 amounted to 13,000 tons per year; however, this figure is probably somewhat greater than actual consumption and with the end of the war the demand dropped substantially. The major advantages of hydrogen fluoride over sulfuric acid in alkylation result from the higher process temperature used and the greater ease of catalyst regeneration. Higher temperature permits of cooling with water rather than by the use of refrigeration. The problem of sludge-acid disposal is serious in many refineries using sulfuric acid; in hydrogen fluoride alkylation, the recovery of acid by distillation is no problem. While the future consumption of hydrogen fluoride for alkylation is uncertain, there is evidence of a gradually increasing requirement for hydrogen fluoride for this purpose, and, further, of the development of new uses for hydrogen fluoride in the petroleum field.

The recently developed use of hydrogen fluoride for the manufacture of uranium hexafluoride is of interest because of its connection with atomic energy and the atomic bomb. In order to separate and concentrate certain uranium isotopes, it was necessary to use a uranium compound that is thermally stable and has a high vapor pressure near room temperature. The only compound meeting this specification is uranium hexafluoride. The reaction of hydrogen fluoride and uranium oxide yields uranium tetrafluoride, which may be further fluorinated with elemental fluorine to the hexafluoride. The quantity of such material produced has not been published (see *Uranium*).

Elsewhere in the inorganic field, hydrofluoric acid finds use in the polishing and etching of glass, and is required in substantial tonnages for the "pickling" of alloy steels (see *Metal surface treatment*). It is used also in the manufacture of a great number of inorganic fluorides (2). Those fluorides that are stable in water are usually prepared by treating the carbonates, oxides, or hydroxides with aqueous hydrofluoric acid, most of the common fluorides falling in this category. Fluorides such as boron trifluoride and antimony pentafluoride, that hydrolyze in water, may be prepared from the chloride by reaction with anhydrous hydrogen fluoride.

A use of hydrogen fluoride, which has been limited in the past but gives promise of substantial increase in the future, is the manufacture of elemental fluorine (see *Fluorine*). The synthetic organic chemical industry offers unbounded opportunity for the development of organic fluorine compounds in many fields of interest. Only a few of current interest can be mentioned here. A number of excellent dyes presumed to be derivatives of benzotrifluoride,  $C_6H_5CF_3$ , have been marketed. The trifluoromethyl group is said to impart stability and light-fastness. Similarly, dyes containing the fluoborate radical have been introduced. Fluorinated hydrocarbons were developed in the search for liquids of unusual thermal and chemical stability for use in the separation of uranium isotopes. Other fluorinated hydrocarbons are being investigated in the effort to produce compounds meeting the specific requirements of various applications; coolants, lubricants, hydraulic fluids, etc. Two fluorine-containing plastics, Teflon and Kel-F, are rapidly finding applications in industry because of their extreme chemical inertness, high thermal stability, and excellent dielectric properties. The number of additional products and uses now being developed is tremendous, and gives full indication of the great promise of fluorine chemistry in the coming years (see *Fluorine compounds, organic*).

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A. S. WOODARD

**Iodine Compounds.** See under "Halogen fluorides," p. 694.

### Iron Compounds.

Both ferrous fluoride,  $\text{FeF}_2$ , and ferric fluoride,  $\text{FeF}_3$ , are known, and also ferrous complexes of the types  $\text{MFeF}_3$  and  $\text{M}_2\text{FeF}_4$  and ferric complexes of the types  $\text{MFeF}_4$ ,  $\text{M}_2\text{FeF}_5$ , and  $\text{M}_3\text{FeF}_6$ .

**Ferric fluoride**,  $\text{FeF}_3$ , formula weight 112.85, forms green rhombic crystals; sp.gr. 3.52. It is sparingly soluble in water (0.091 gram/100 ml. at  $25^\circ\text{C}$ .) but soluble in acids. Ferric fluoride is formed by heating anhydrous ferric chloride in a stream of hydrogen fluoride. It is said to be used in the manufacture of porcelain and pottery.

F. D. LOOMIS

### Lead Compounds.

**Lead fluoride**,  $\text{PbF}_2$ , formula weight 245.21, is a white rhombic solid; m.p.  $855^\circ\text{C}$ .; b.p.  $1290^\circ\text{C}$ .; sp.gr. 8.24. It is sparingly soluble in water (0.066 gram/100 ml. at  $25^\circ\text{C}$ .); it is somewhat more soluble in nitric acid but insoluble in other acids. It is reportedly used as an ingredient of underwater paints, in the manufacture of special glasses, and for the preparation of lead tetrafluoride.

**Lead tetrafluoride**,  $\text{PbF}_4$ , formula weight 283.21, a light yellow crystalline solid that melts at  $600^\circ\text{C}$ . and is decomposed by water into lead dioxide,  $\text{PbO}_2$ , has been used in organic fluorinations.

F. D. LOOMIS

### Lithium Fluoride.

Lithium fluoride,  $\text{LiF}$ , formula weight 25.94, is a fluffy white crystalline (cubic) powder; m.p.  $847^\circ\text{C}$ .; b.p.  $1680^\circ\text{C}$ .; sp.gr. 2.64;  $n_D$  1.3915; sp.heat, 0.373 cal./gram at  $10^\circ\text{C}$ . The salt is sparingly soluble in water (0.133 gram/100 ml. at  $25^\circ\text{C}$ .), insoluble in alcohol and other organic solvents, and soluble in acids including hydrofluoric acid, with which it forms the bifluoride,  $\text{LiHF}_2$ . With lithium hydroxide, the fluoride forms  $\text{LiF} \cdot \text{LiOH}$ , which melts at  $462^\circ\text{C}$ . Lithium fluoride is made from lithium hydroxide and aqueous hydrofluoric acid. Owing to the relative insolubility of lithium carbonate in water, to the tendency of lithium fluoride to adsorb appreciable quantities of lithium carbonate, and to the fact that aqueous hydrofluoric acid is feebly ionized, lithium fluoride of high purity can be obtained from lithium carbonate and hydrofluoric acid only with great difficulty. It is used as a constituent of aluminum welding fluxes and in the manufacture of enamels and glazes, especially leadless pottery glazes.

F. D. LOOMIS

### Magnesium Fluoride.

Magnesium fluoride,  $\text{MgF}_2$ , formula weight 62.32, occurs in nature as the mineral sellaite; m.p.  $1260^\circ\text{C}$ .; b.p.  $2260^\circ\text{C}$ .; sp.gr. 3.127;  $n_D^{20}$  1.378, 1.390; solubility in water, 0.013 gram/100 ml. at  $25^\circ\text{C}$ . Magnesium fluoride is formed as a colorless crystalline (tetragonal) powder by the interaction of magnesium oxide and hydrofluoric acid. Its production by the reaction of magnesium chloride with fluorspar has been

patented. Magnesium fluoride is used as a cover flux in the metallurgy of magnesium; in fluxes for chinaware, porcelain, and pottery; and as a coating agent for titanium pigments. A very pure grade is used to improve the light transmission (antireflecting characteristics) of optical and plate glass.

F. D. LOOMIS

**Mercury Compounds.** See *Fluorine compounds, organic*, p. 738.

### Nickel Fluoride.

Nickel fluoride,  $\text{NiF}_2$ , formula weight 96.69, forms green tetragonal crystals; sp.gr. 4.63. The salt is slightly soluble in water (2.6 grams/100 ml. saturated solution at  $20^\circ\text{C}.$ ), soluble in potassium cyanide, hot ammonium fluoride solutions, and aqueous hydrofluoric acid, but insoluble in other acids and alcohol. It is formed when a solution of nickel carbonate in aqueous hydrofluoric acid is evaporated. Its limited use in electroplating baths has been reported.

F. D. LOOMIS

**Niobium Compounds.** See *Columbium compounds*, Vol. 4, p. 321.

### Nitrogen Trifluoride.

Nitrogen trifluoride,  $\text{NF}_3$ , formula weight 71.01, is a colorless gas; m.p.,  $-208.5^\circ\text{C}.$  (there is a transition point at  $-219^\circ\text{C}.$ ); b.p.,  $-119^\circ\text{C}.$ ;  $d_4^{-129}$  (liquid), 1.537; heat of formation, approx. 26,000 cal./gram-mole; latent heat of vaporization at  $-273.1^\circ\text{C}.$ , 3,028 cal./gram-mole. Nitrogen trifluoride is much more stable than the other nitrogen halides and is nonexplosive. It does not react with water or caustic alkalis and does not attack dry glass, mercury, or manganese dioxide. Nitrogen trifluoride is best prepared by electrolysis of molten ammonium bifluoride at as low a temperature as possible, because the fluorides  $\text{NF}_2$ ,  $\text{NHF}_2$ , and  $\text{NH}_2\text{F}$ , which are also formed in small amounts, decompose explosively above  $100^\circ\text{C}.$  The impure product is usually passed over manganese dioxide to destroy these impurities.

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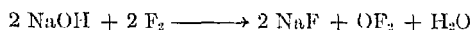
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### Oxygen Compounds.

The two compounds of oxygen and fluorine definitely known,  $\text{OF}_2$  and  $\text{O}_2\text{F}_2$ , are often called fluorine oxides by analogy with other halogen oxides. Actually, however, they are oxygen fluorides, because fluorine is more electronegative than oxygen.

**Oxygen fluoride** (fluorine monoxide),  $\text{OF}_2$ , formula weight 54.00, is a colorless gas when pure; m.p.,  $-223.8^\circ\text{C}.$ ; b.p.,  $-144.8^\circ\text{C}.$ ;  $d_4^{-223.8}$  (liquid), 1.90; crit. temp.,  $-81^\circ\text{C}.$ ; heat of formation, approx.  $-7,000$  cal./gram-mole; heat of vaporization,

−2,508 cal./gram-mole; free energy of formation at 25°C., approx. 11,000 cal./gram-mole; entropy at 25°C., approx. 58 cal./gram-mole/°C.; soly. at 0°C., 6.8 ml./100 ml. water. The most striking property of this substance is that it is not explosive at temperatures below its boiling point, whereas chlorine monoxide, Cl<sub>2</sub>O, is very unstable. Solutions of oxygen fluoride have no acidic properties but have very strong oxidizing properties. Oxygen fluoride is decomposed by most metals on heating, forming fluorides and oxides. The gas does not attack dry glass or quartz at ordinary temperatures, but mercury is attacked. Oxygen fluoride is prepared by passing gaseous fluorine through a dilute solution of sodium hydroxide:



**Dioxygen difluoride**, O<sub>2</sub>F<sub>2</sub>, formula weight 70.00, is a brown gas; m.p., −163.5°C.; vapor pressure at −86°C., approx. 162 mm. Hg; sp.gr. (solid) at −163.5°C., 1.912. It is formed by pumping an equimolecular mixture of fluorine and oxygen at a pressure of 15–20 mm. through a quartz discharge tube cooled in liquid air. This oxide separates as a yellow solid that can be distilled unchanged at temperatures below −100°C. Above this temperature, it decomposes into its elements.

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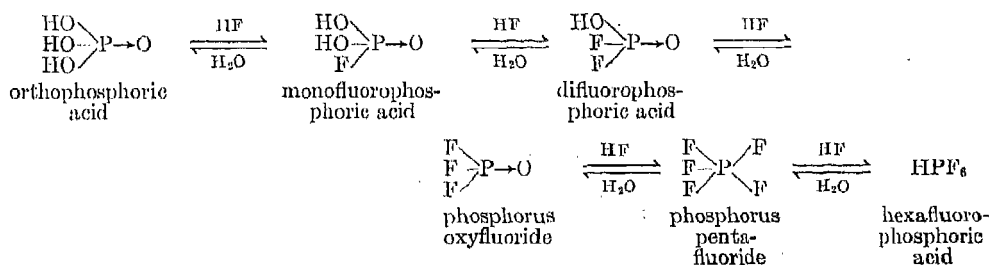
## Phosphorus Compounds.

### Phosphorus Fluorides.

The simple fluorides, PF<sub>3</sub> and PF<sub>5</sub>, and the oxy- and sulfofluorides (phosphoryl and thiophosphoryl fluorides), POF<sub>3</sub> and PSF<sub>3</sub>, are colorless gases, which (except for the trifluoride) fume strongly in moist air. Mixed halides are also known, such as PF<sub>2</sub>Cl, PFCl<sub>2</sub>, PF<sub>3</sub>Cl<sub>2</sub>, POF<sub>2</sub>Cl, POFCl<sub>2</sub>, PSF<sub>2</sub>Cl, and PSFCl<sub>2</sub>, and the corresponding fluoride bromides. See *Phosphorus compounds*.

### Fluorophosphoric Acids (Fluophosphoric Acids).

The fluorophosphoric (or fluophosphoric) compounds (sometimes called the FP compounds) may be considered to be derived from various orthophosphates through substitution of fluorine for oxygen or hydroxyl groups. The interrelationships (but not necessarily the methods of preparation) of the acids are indicated as follows:



Hexafluorophosphoric acid exists only in solution, the  $\text{PF}_6^-$  ion resulting from the coordination of the fluoride ion with phosphorus pentafluoride. Similarly the fluorophosphates are related to orthophosphates, and the hexafluorophosphates are coordination compounds of the metal fluorides with phosphorus pentafluoride. The esters of monofluorophosphoric acid are of considerable interest. A few esters of difluorophosphoric acid have been prepared, but, in general, these are unstable and of no importance. At present, no hexafluorophosphoric esters are known.

Mono- and difluorophosphoric acids may be prepared as anhydrous liquids, which are quite stable. Monofluorophosphoric acid resembles concentrated sulfuric acid in viscosity, specific gravity, volatility, and lack of corrosiveness toward glass. Difluorophosphoric acid is volatile, less dense than the mono acid, mobile, and strongly fuming. Hexafluorophosphoric acid, in 65% solution, fumes about as much as does 50% hydrofluoric acid. The solution contains difluorophosphoric, hydrofluoric, and other acids in equilibrium with the hexafluorophosphoric acid; hence it has some of the properties of aqueous hydrofluoric acid and cannot be used in glass.

In alkaline solutions, the  $\text{PO}_3\text{F}^{2-}$  and  $\text{PF}_6^-$  ions (especially the latter) are stable toward hydrolysis, whereas the fluosilicate, fluoborate, and fluosulfonate ions are not (8). Solutions of alkali metal mono- and hexafluorophosphates are neutral and remain so indefinitely. The  $\text{PO}_2\text{F}_2^-$  ion is less stable than the other fluorophosphate ions and yields  $\text{PO}_3\text{F}^{2-}$  and  $\text{F}^-$  by reaction with water. In acidic mediums, all of the fluorophosphate ions hydrolyze more or less rapidly, depending on the temperature and concentration.

The fluorophosphoric compounds constitute a relatively new and undeveloped group of chemicals. The existence of a fluorophosphate ion was discovered in 1927 by Lange (5), who with his co-workers continued to explore the field. Pronounced physiological effects of the dialkyl esters reported by these workers (7) led to a very considerable amount of research by British and American scientists during World War II (11). Diisopropyl monofluorophosphate was found to be a particularly potent inhibitor for cholinesterase, an enzyme essential for normal nerve functioning. In recent years, the commercial development of the fluorophosphates has been undertaken by the Ozark-Mahoning Company for applications as catalysts, electrobrightening agents, fluxes, fungicides, insecticides against moths, dental-caries inhibitors, and medicinals.

*Equipment.* For storage and use of the anhydrous di- and concentrated hexafluorophosphoric acids, aluminum is satisfactory. The anhydrous mono acid also may be used in aluminum at ordinary or slightly elevated temperatures, although when it has an excess of phosphoric acid, it will react with aluminum. Dilute aqueous solutions of any of these acids will dissolve aluminum. Magnesium apparently is suitable under the same conditions as aluminum and, in addition, should be usable in dilute solutions of hexafluorophosphoric acid, which are corrosive to aluminum. Stainless steels may frequently be satisfactorily used with aqueous solutions and for short-time contacts with concentrated or anhydrous acids. The same is true of nickel and copper and their alloys. For dilute solutions lead equipment or linings may be used. Silver and platinum are universally acceptable from the standpoint of chemical inertness.

For laboratory-scale experiments, Pyrex equipment may be used with monofluorophosphoric acid and also with the di acid at temperatures below 50°C. and in the absence of moisture. Polystyrene and polyethylene containers are useful at temperatures below about 70°C.; the latter is generally better because of its lower porosity.

Saran tubing and linings appear to be satisfactorily resistant. Teflon, Kel-F, and Fluorothene are resistant; gaskets and packings of these materials frequently are desirable. Rubber (either natural or neoprene) contributes color to clear anhydrous or concentrated acids, and hence is unsatisfactory for these, but it is useful for dilute solutions. Butyl rubber is superior and may be used with anhydrous acids. Impregnated carbon and Haveg 48 appear satisfactory for all concentrations of the fluorophosphoric acids. Coatings of paraffin or ceresin waxes are sufficiently inert to be usable.

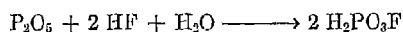
**Hazards.** Experience and animal experiments indicate that the fluorophosphoric acids are much less toxic and dangerous than hydrogen fluoride (2). Nevertheless, they should be handled with great care. Monofluorophosphoric acid may be on the skin for several minutes without producing a burn, and no penetration to underlying tissues occurs to produce deep-seated injuries. Contact of liquid difluorophosphoric acid with the skin will cause burns unless prompt removal and treatment are effected. Washing with water followed by ample applications of a thin slurry of magnesia will usually prevent injury. In some cases, the subcutaneous injection of calcium gluconate may be advisable. The copious fumes of difluorophosphoric acid are irritating but not particularly toxic. With hexafluorophosphoric acid also, contact with the solution and inhalation of fumes should be avoided, although even with this high-fluorine acid typical hydrogen fluoride burns have never been observed.

**Monofluorophosphoric acid**,  $\text{H}_2\text{PO}_3\text{F}$  or  $(\text{HO})_2\text{POF}$ , formula weight 100.00, is a colorless, nonvolatile, viscous liquid with little odor.

**Properties.** Monofluorophosphoric acid has no definite melting point and is completely soluble in water;  $d_4^{25}$ , 1.818.

An aqueous solution shows the normal behavior of a dibasic acid with the first neutralization point in 0.05 *N* solution at pH 3.5 and the second at pH 8.5. The permanent end point indicates the stability of the  $\text{PO}_3\text{F}^{2-}$  ion at this pH. Slow hydrolysis occurs at low pH to give orthophosphoric and hydrofluoric acids. Anhydrous acid causes rapid swelling of cellulose. No oxidizing characteristics are shown by the acid. The anhydrous acid acts as a polymerization catalyst.

**Preparation.** One of the usual methods for preparing anhydrous monofluorophosphoric acid involves the use of 69% aqueous hydrofluoric acid and phosphorus pentoxide (phosphoric anhydride),  $\text{P}_2\text{O}_5$  ( $\text{P}_4\text{O}_{10}$ ) (see *Phosphorus compounds*). The reaction is most simply represented by the equation:



In practice a product having as much as 20% each of orthophosphoric and difluorophosphoric acids is commonly obtained.

Theoretically, it is as convenient to use anhydrous hydrogen fluoride with metaphosphoric acid:



but practically this reaction is less satisfactory because of difficulty in preparing pure metaphosphoric acid and because of its tendency to become glassy or sticky so that it does not dissolve completely in the hydrogen fluoride.

Monofluorophosphoric acid is also always obtained in the preparation of the difluoro acid (see p. 715).

For the reaction of phosphorus pentoxide and anhydrous, or even 69%, hydrogen



fluoride, it is essential that the phosphorus pentoxide be kept dry. Hydrogen fluoride is of course corrosive and somewhat hazardous to handle. The heat of reaction is high and must be dissipated. No purification of the product is possible since monofluorophosphoric acid cannot be distilled; hence, for a high-quality acid the right proportions of pure reactants are necessary. Finally, the mono acid itself is corrosive to some metals and other construction materials, so the equipment must be properly chosen.

In pilot-plant production pure silver has been generally used. A 5-gal. reactor with a screw-in plug closure and a Teflon gasket is charged with the phosphorus pentoxide. Then the plug is screwed in and the vessel is evacuated through a silver tube in the plug; the reactor is placed in a rocking device, and the stoichiometric amount of hydrogen fluoride is allowed to flow in slowly from another, smaller silver container, which is also secured in the rocker. Cooling is effected by flowing water over the larger vessel. To insure solution of all of the oxide, some of which may be initially transformed into sticky masses of partially hydrated and reacted material, the temperature is permitted finally to go to about 150°C.

For larger operations type 316 stainless steel and 3S aluminum equipment has been used. In the former there will usually be a development of a brown coloration in the product, and the latter is susceptible to attack at elevated temperatures, especially during the addition of the hydrogen fluoride when the phosphorus pentoxide (or its hydration products) is in excess.

Laboratory experimental lots of monofluorophosphoric acid are packaged and shipped in polystyrene or polyethylene bottles in sizes up to 2-lb. capacity. Larger quantities are transported in aluminum drums (I.C.C. 42B, C, or D) in sizes up to 55 gal. Shipments must bear the I.C.C. white label.

*Analysis.* The  $\text{PO}_3\text{F}^{2-}$  content of an acid is determined by precipitation of silver monofluorophosphate from a neutral solution containing 80% ethyl alcohol and by subsequent distillation of this precipitate with perchloric acid,  $\text{HClO}_4$ , for fluorine determination. The latter step is necessary because other phosphates will precipitate with the silver ion. Free fluoride ion, however, does not precipitate. Orthophosphoric acid contamination is determined by precipitation of silver phosphate from a dilute neutral solution with subsequent titration of the excess silver with potassium thiocyanate. Gravimetric estimation of the  $\text{PO}_2\text{F}_2^-$  content can be made by use of nitron (2,5,6-triphenyl-2,3,5,6-tetrazabicyclo[2.1.1]-3-hexene). Total fluorine is found by a distillation at 135°C. with perchloric acid and subsequent titration with thorium nitrate. For determining total phosphorus, a sample is digested with nitric acid to effect complete conversion to  $\text{PO}_4^{3-}$  which is then precipitated with silver nitrate for a Volhard titration. Soluble salts are assayed similarly to the acid, and insoluble salts only by determination of total fluorine and total phosphorus.

*Uses.* Although patents have been granted on the use of the monofluorophosphoric acid as a catalyst for polymerization of olefins (15) and in combination with boron trifluoride for alkylation of isoparaffins (16), these possible applications have not resulted to date in commercial production. The acid has metal-cleaning and fungicidal properties of possible importance.

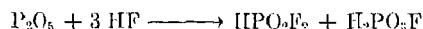
**Difluorophosphoric acid**,  $\text{HPO}_2\text{F}_2$  or  $\text{HOPOF}_2$ , formula weight 101.99, is a mobile, strongly fuming, colorless, clear liquid with irritating fumes.

*Properties.* M.p., -75°C.;  $b_{760}$ , 116°C.;  $b_{100}$ , 51°C.;  $d_4^{25}$ , 1.583; vapor pressure (50–90°C.),  $\log p_{\text{mm.}} = 1732.2/T + 7.332$ ; heat of vaporization, 7925 cal./gram-mole.

A freshly made solution behaves as a strong monobasic acid; on neutralization, the

end point is at about pH 7.3. Neutralized solutions slowly become acidic because of hydrolysis to monofluorophosphoric and hydrofluoric acids. The anhydrous acid undergoes slow decomposition on distillation at atmospheric pressure, reacts with alcohols to give monofluorophosphoric acid esters, and is a polymerization catalyst.

*Preparation.* In the usual procedure, anhydrous phosphorus pentoxide is treated with hydrogen fluoride to give an equimolecular mixture of mono- and difluorophosphoric acids:



From the acid mixture the difluoro acid is recovered in high purity by distillation at a reduced pressure. Excess hydrogen fluoride may be collected in the distillate if too much has been used in the original mixture or if not enough care is taken during the distillation to prevent condensation of the more volatile hydrogen fluoride along with the difluorophosphoric acid.

Silver, aluminum, or stainless-steel equipment may be used for the reaction and the distillation. If the difluoro acid remains for several days in contact with stainless steel, it will usually become discolored through solution of small amounts of the alloy components.

Shipping containers and regulations are the same as for monofluorophosphoric acid.

*Analysis.* Because of the tendency toward hydrolysis when difluorophosphoric acid is dissolved in water, a chemical assay is not entirely satisfactory. However, if a weighed, cold sample of acid is poured directly into a cold solution of nitron acetate, a reasonably precise value for difluoro acid content may be obtained. Total fluorine and total phosphorus are obtainable by the procedures used for monofluorophosphoric acid.

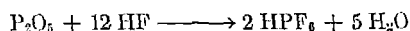
*Uses.* The situation with difluorophosphoric acid is about the same as with the mono acid. The difluoro acid is known to be catalytic in various polymerization reactions, but it has not achieved commercial adoption because of its relatively high cost.

**Hexafluorophosphoric acid**,  $\text{HPF}_6$ , formula weight 145.99, is a colorless, clear liquid which fumes considerably. The approximate composition of the concentrated acid ("FP Acid No. 3") is:  $\text{HPF}_6$ , 65%; HF, 6%; mixture of  $\text{HPO}_2\text{F}_2$ ,  $\text{H}_2\text{PO}_3\text{F}$ , and  $\text{H}_3\text{PO}_4$ , 8%; water, 21%.

*Properties* (of FP Acid No. 3). Sp.gr., 1.65 (approx.).

Hexafluorophosphoric acid acts as a strong monobasic acid. It hydrolyzes slowly when diluted to give other fluorophosphoric acids and finally orthophosphoric and hydrofluoric acids. In concentrated solutions, however, the hexafluoro acid establishes equilibrium with its hydrolysis products present in relatively low concentrations. At least two hydrates (the hexa and octa) can be prepared by cooling mixtures containing the acid and water in proper concentrations. The hexahydrate melts at 31°C.

*Preparation.* Phosphorus pentoxide and anhydrous hydrogen fluoride react in accordance with the equation:



The reaction must take place in a closed system to prevent loss of volatile matter. Aluminum equipment, as well as silver, may be used.

The theoretical concentration of hexafluorophosphoric acid (76.5%) is not reached because of the presence of other fluorophosphoric acids and uncombined orthophosphoric and hydrofluoric acids.

Shipping containers and regulations are the same as for monofluorophosphoric acid.

*Analysis.* The  $\text{PF}_6^-$  content is determined by use of nitron or tetraphenylarsonium chloride, either one of which gives slightly soluble precipitates suitable for gravimetric determinations. To prevent interference from  $\text{PO}_2\text{F}_2^-$  ions which will also precipitate, the test solutions should be made alkaline and boiled for a few minutes to hydrolyze the difluorophosphate; the  $\text{PF}_6^-$  ion will not be affected. Soluble salts are similarly assayed, and insoluble salts are assayed by the determination of total fluorine and total phosphorus.

*Uses.* Several salts of hexafluorophosphoric acid are made by neutralization of the acid and have some commercial possibilities. The acid in solution in dilute sulfuric acid gives good electrolytic polishing of stainless steels (10).

### Fluorophosphoric Acid Salts

**Monofluorophosphates.** The present stage of development of the monofluorophosphates is indicated in Table I. The monofluorophosphates have certain similarities to the corresponding sulfates, just as monofluorophosphoric acid resembles sulfuric acid in some respects. Some of the salts are isomorphous with the sulfates. Variations in solubility are generally closely similar in the two series of salts. Also, alum-like double salts are obtainable from the monofluorophosphates.

TABLE I. Monofluorophosphates.

Available in laboratory or pilot-plant quantities	Others described in reference (6)	Described in reference (8)
$\text{Li}_2\text{PO}_3\text{F}$	$(\text{NH}_4)_2\text{PO}_3\text{F}$	$\text{NiPO}_3\text{F} \cdot 7\text{H}_2\text{O}$
$\text{Na}_2\text{PO}_3\text{F}$	$\text{NH}_4\text{HPO}_3\text{F}$	$\text{CoPO}_3\text{F} \cdot 6\text{H}_2\text{O}$
$\text{K}_2\text{PO}_3\text{F}$	$\text{SrPO}_3\text{F} \cdot \text{H}_2\text{O}$	$\text{CuPO}_3\text{F} \cdot 5\text{H}_2\text{O}$
$\text{Ag}_2\text{PO}_3\text{F}$	$\text{Hg}_2\text{PO}_3\text{F}$	$\text{ZnPO}_3\text{F} \cdot 5\text{H}_2\text{O}$
$\text{CaPO}_3\text{F} \cdot 2\text{H}_2\text{O}$	$\text{PbPO}_3\text{F}$	$\text{NiPO}_3\text{F} \cdot (\text{NH}_4)_2\text{PO}_3\text{F} \cdot 6\text{H}_2\text{O}$
$\text{BaPO}_3\text{F}$	$(\text{H}_2\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{NH}_2)\text{H}_2\text{PO}_3\text{F}$	$\text{CoPO}_3\text{F} \cdot (\text{NH}_4)_2\text{PO}_3\text{F} \cdot 6\text{H}_2\text{O}$
		$\text{Al}_2(\text{PO}_3\text{F})_3 \cdot (\text{NH}_4)_2\text{PO}_3\text{F} \cdot 24\text{H}_2\text{O}$

The alkali metal monofluorophosphates are water-soluble, neutral, stable, colorless salts. Solutions of 1% concentration hydrolyze less than 1% per hour, even at 95°C.; at room temperature they are perfectly stable unless acid or some cation giving an insoluble fluoride is added. At and above their melting points these salts slowly lose fluorine-containing vapors through thermal or hydrolytic decomposition. The salts have lower animal toxicity than simple fluorides but have greater fungicidal and bactericidal potencies. They inhibit dental caries in hamsters at least as effectively as do simple fluorides (12).

The alkaline earth monofluorophosphates are only slightly soluble in water and are somewhat susceptible to thermal and hydrolytic decompositions.

Neutralization of the appropriate base by monofluorophosphoric acid is the basis for one method of making the salts. Because of contamination from orthophosphoric and difluorophosphoric acids in the monofluoro acid, this procedure has obvious disadvantages. High-purity sodium and potassium monofluorophosphates can be made by fusing stoichiometric mixtures of the fluoride and metaphosphate (17). A temperature of about 700°C. is necessary for the sodium salt and about 900°C. for the potas-

sium. A platinum, silver, or graphite retort is satisfactory; it should be tightly covered to prevent decomposition of the molten salts.

The slightly soluble monofluorophosphates are conveniently produced by metathesis; for example:



Another method is given in reference (4).

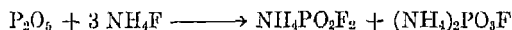
Possible fungicidal, bactericidal, dental hygienic, metal fluxing, and ceramic applications of the monofluorophosphates show some promise of developing commercial-scale production.

*Sodium monofluorophosphate*,  $\text{Na}_2\text{PO}_3\text{F}$ , formula weight 143.97, m.p. 625°C. (approx.), when melted, is very fluid and reactive toward metal surfaces. About 25 grams is soluble in 100 grams water at room temperature. The LD<sub>50</sub> by intraperitoneal injection into 200–300 gram rats is 220 mg./kg.; the LD<sub>50</sub> by oral administration is 570 mg./kg. (on a fluorine content basis, the  $\text{Na}_2\text{PO}_3\text{F}$  is about one-third as toxic as sodium fluoride). The salt prevents dental caries in hamsters when used in their drinking water in concentration to give 20 p.p.m. of fluorine. *Aspergillus niger*, *Staphylococcus aureus*, *Salmonella typhosa*, *Pseudomonas aeruginosa*, and *Neisseria catarrhalis* organisms are inhibited by 1% concentrations of sodium monofluorophosphate.

*Calcium monofluorophosphate dihydrate*,  $\text{CaPO}_3\text{F} \cdot 2\text{H}_2\text{O}$ , formula weight 174.09, decomposes without melting; the solubility in water at 20°C. is about 1 gram per 100 grams of water. The dihydrate is stable at 100°C. but loses its water at about 170°C. Additional decomposition occurs at about 400°C.

**Difluorophosphates** have had very little attention. They seem to have little commercial appeal because of the hydrolytic instability of the  $\text{PO}_2\text{F}^-$  ion.

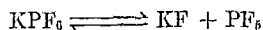
*Ammonium difluorophosphate*,  $\text{NH}_4\text{PO}_2\text{F}_2$ , formula weight 119.02, m.p. 213°C., is very soluble in water. The solution hydrolyzes to give the monofluorophosphate. The mono- and difluorophosphates can be prepared together:



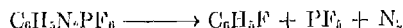
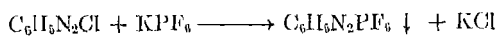
The ammonium difluorophosphate can be extracted from the mixture by use of boiling alcohol (9).

Potassium and cesium difluorophosphates are soluble in water. Insoluble nitron, strychnine, brucine, morphine, cocaine, and tetramethylammonium salts have been described.

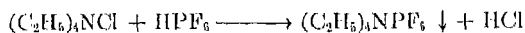
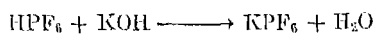
**Hexafluorophosphates.** A number of hexafluorophosphates have been made. In general, these salts resemble the perchlorates. Many are very soluble in water; some of these extremely soluble salts cannot be crystallized from solution without decomposition. Substituted ammonium salts are generally insoluble in water. Boiling in dilute alkaline solutions does not cause decomposition of hexafluorophosphates and only by fusion with the caustic is the  $\text{PF}_6^-$  ion completely broken up. Generally speaking, the hexafluorophosphates dissociate when heated to their melting points to give phosphorus pentafluoride as one product. This gas can be conveniently prepared from potassium hexafluorophosphate in this way:



For a small-scale laboratory preparation, precipitating a diazonium hexafluorophosphate, drying it, and then heating to get a steady flow of phosphorus pentafluoride may be more convenient:



The soluble, stable salts are produced by interaction of the hexafluorophosphoric acid and the appropriate base with subsequent evaporation to crystallization. The insoluble salts may be made by metathesis between the hexa acid or a soluble salt thereof and a soluble salt of the desired base. For example:



Another method of preparation is given in reference (14).

The commercial possibilities of the hexa salts have been explored only slightly. Applications may be found for them in fluxes, in glass-etching mixtures, in preparation of phosphorus pentafluoride, in producing protective atmospheres for metal-annealing furnaces, etc.

*Potassium hexafluorophosphate*,  $\text{KPF}_6$ , formula weight 184.1, m.p.  $575^\circ\text{C}$ . (approx.) (dec.). The solubility in water at  $0^\circ\text{C}$ . is about 5.5 grams per 100 grams of solvent; at  $25^\circ$ , 9.3 grams; and at  $50^\circ$ , 20.6 grams. Solutions are neutral, noncorrosive, and stable. The salt is of very low toxicity toward animals and microorganisms.

*Ammonium hexafluorophosphate fluoride*,  $\text{NH}_4\text{PF}_6 \cdot \text{NH}_4\text{F}$ , formula weight 200.06, crystallizes when concentrated hexafluorophosphoric acid is neutralized with ammonium hydroxide. The dried flaky crystals are stable until heated to about  $140^\circ\text{C}$ ., whereupon they sublime. The vapors attack glass; the solid does not. The ammonium fluoride portion may be determined by titration of a solution of the double salt with standard thorium nitrate.

*Insoluble Salts.* Various substituted ammonium, pyridinium, and alkaloidal hexafluorophosphates have been prepared. They are of low water solubility. Examples are: hexafluorophosphates of tetraethylammonium, benzyltrimethylammonium, cetyl-dimethylbenzylammonium, pyridinium, picolinium, benzenediazonium, and strychninium.

*Soluble but Unisolable Salts.* Calcium and barium hexafluorophosphates have not been isolated as dry salts of high purity. Solutions can be obtained and are of usual stability, but evaporation, even at temperatures near  $0^\circ\text{C}$ ., is accompanied by hydrolysis when saturation is approached. The sodium salt can be crystallized out as a hydrate but care is necessary to prevent extensive hydrolysis.

*Other Salts.* Various amines and similar compounds have been reported. These include:  $[\text{Cu}(\text{en})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{PF}_6)_2 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ ,  $\text{Co}(\text{PF}_6)_2 \cdot 6\text{NH}_3$ , and  $\text{Ni}(\text{PF}_6)_2 \cdot 6\text{NH}_3$ .

The fact that certain sterols give crystalline salts with hexafluorophosphoric acid has been recently reported. These unusual compounds may be of importance in separating mixtures of steroids.

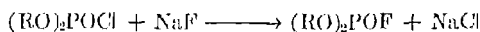
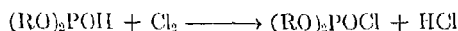
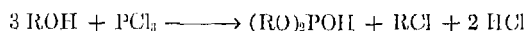
### Fluorophosphoric Acid Esters

The only compounds of importance in this group are the monofluorophosphoric esters: neutral or normal,  $(\text{RO})_2\text{POF}$ , and acid or half-esters,  $(\text{RO})(\text{HO})\text{POF}$ . Hexafluorophosphoric esters apparently cannot exist because of the ionic coordinative re-

quirements of the  $\text{PF}_6^-$  ion. Difluorophosphoric esters such as  $\text{C}_2\text{H}_5\text{OPOF}_2$  have been prepared, but they are so readily hydrolyzed to monofluorophosphoric esters that they seem to be of little importance. A thiodifluorophosphoric ester,  $\text{C}_2\text{H}_5\text{OPSF}_2$ , has been reported as resistant to hydrolysis but subject to rapid oxidation in the air.

**Neutral Monofluorophosphoric Esters.** The neutral esters are extremely toxic. They became of great significance during World War II after it had been recognized by a British research team that their toxicity was a result of their cholinesterase-inhibiting activity, which made them typical nerve gases, and that the diisopropyl ester, usually called DFP, was the most potent compound of the group:

The neutral esters were first obtained by heating silver monofluorophosphate with alkyl iodides under pressure. An improved method involved carrying out the reaction in the presence of a solvent under reflux. A still more convenient procedure was evolved in accordance with the following equations (11):



When isopropyl alcohol was used, diisopropyl hydrogen phosphite was obtained in an 89% yield. Subsequent chlorination gave 76% of the monochlorophosphate. This compound, dissolved in dry benzene, was heated with dry sodium fluoride and yielded 90% DFP. This was operated virtually as a one-stage process and pure DFP was obtained in an overall yield of 75% (11).

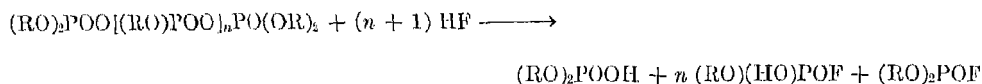
TABLE II. Characteristics of Dialkyl Monofluorophosphates and of Sodium Isopropyl Monofluorophosphate.

	$(\text{CH}_3\text{O})_2\text{POF}$	$(\text{C}_2\text{H}_5\text{O})_2\text{POF}$	$(\text{iso-C}_3\text{H}_7\text{O})_2\text{POF}^a$	$(\text{iso-C}_3\text{H}_7\text{O})(\text{NaO})\text{POF}$
Formula wt. ....	128.05	156.10	184.15	164.06
Physical state .....	Liquid	Liquid	Liquid	Solid
B.p., °C. ....	149	170	63-66 <sub>10</sub>	—
Sp.gr. ....	1.28 (approx.)	1.15	1.07	—
Solubility .....	Sol. in alcohol, acetone, ether; fairly sol. in water	Sol. in alcohol, acetone, ether; fairly sol. in water	Sol. in organic solvents, insol. in water	Insol. in organic solvents, sol. in water
Vapor pressure at 20°C., mm. ....	4.11	1.47	0.97	—
Concn. satd. vapor at 20°C., mg./liter. ....	28.7	12.5	9.7	—
Concn. detectable by odor, mg./liter. ....	0.18	0.15	0.36	—
Effects on humans of trace of vapor. ....	Tightness of chest, miosis, toxicity comparable to hydrogen cyanide			—
LC <sub>50</sub> for mice, 10-min. exposure, mg./liter. ....	0.29	0.50	0.60	—
LD <sub>50</sub> for mice, intraperitoneal injection, mg./kg. ....	—	—	4	350
Cholinesterase inhibitory power, molarity giving 50% inhibition .....	—	$8.0 \times 10^{-9}$	$1.3 \times 10^{-9}$	$2.9 \times 10^{-11}$

<sup>a</sup> Source: reference (13); values for the cholinesterase inhibitory power from H. M. Fitch, New York University-Bellevue Medical Center.

Some properties of three of the dialkyl esters are given in Table II. Many other alkyl fluorophosphoric esters and some aryl esters were made in the extensive investigations during World War II, but the principal interest now is centered in the diisopropyl compound. It is of unique medicinal applicability in severe cases of glaucoma, for which purpose it is marketed as a 0.1% solution in peanut oil under the trade name Floropryl. Experimental applications in myasthenia gravis and in paralytic ileus have given promising results.

**Acid Monofluorophosphoric Esters.** Possible medical applications of DFP stimulated investigations of water-soluble esters, which might have advantages over the oil-soluble, water-insoluble DFP. The desired solubility is found in the half-esters or acid esters of the type (RO)(HO)POF, which can be easily prepared by treating alkyl polyphosphates with anhydrous hydrogen fluoride as in the equation:



It is obvious that when  $n$  is large, the products from the phosphorus atoms at each end become relatively inconsequential. Ordinarily, however, the dialkyl ester may be separated from the mixture by fractional distillation; the monoalkyl ester may be distilled at low pressures, but is not easily separated from the dialkyl orthophosphate.

The acid esters are strongly acidic and yield alkali metal salts by neutralization and subsequent evaporation of the solution at low temperatures. These salts of the esters are at least as stable as the salts of monofluorophosphoric acid itself. The toxicity and the cholinesterase inhibitory power are very much lessened by replacement of an isopropyl group by sodium (see Table II), and it appears that applications for the half-esters in the medicinal field are improbable.

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WAYNE E. WHITE

**Platinum-Group-Metal Fluorides.** See *Platinum-group-metal compounds*.

**Potassium Compounds.**

**Potassium fluoride**, KF, formula weight 58.10, is a white hygroscopic solid that crystallizes in the cubic system; m.p. 859.9°C.; b.p. 1505°C.; sp.gr. 2.481. The salt is readily soluble in water; its solubility is 92.3 grams/100 grams water at 18°C. and 96.4 at 21°C. The salt forms two hydrates: potassium fluoride dihydrate,  $\text{KF} \cdot 2\text{H}_2\text{O}$ , crystallizes in the monoclinic system and melts at 41°C.; the tetrahydrate,  $\text{KF} \cdot 4\text{H}_2\text{O}$ , melts at 19.3°C.

Potassium fluoride is prepared commercially by neutralizing hydrofluoric acid with potassium carbonate. The resultant solution is evaporated and cooled. If the anhydrous salt is desired, the cooling is stopped at 50–55°C., and the crystals are separated by centrifuging at this temperature. If the dihydrate is desired, the solution is cooled to room temperature, and the resultant crystals are centrifuged and packaged as a moist crystal. The anhydrous salt is also prepared by boiling the prepared solution to dryness. Extreme care is necessary in handling the anhydrous salt to prevent hydration.

The anhydrous salt is used in organic synthesis for the introduction of fluorine. Both the anhydrous salt and the dihydrate are used in preparing solder fluxes.

**Potassium bifluoride** (potassium hydrogen fluoride, potassium acid fluoride, Frémy's salt),  $\text{KHF}_2$ , formula weight 78.11, is a white crystalline salt with a slightly acid odor. Its excellent solvent action for metallic oxides is the basis for its use in solder flux compositions. It is one of the essential components of electrolytes for the preparation of fluorine.

*Properties.* Potassium bifluoride freezes to a soft solid at 239°C. At 195°C. a transformation takes place, and a hard white solid results. Below 195°C. the  $\alpha$ -form is the stable phase, and between 195°C. and 239°C. the  $\beta$ -form is stable (3). It decomposes at higher temperatures to hydrogen fluoride and potassium fluoride. The heat of formation from hydrofluoric acid and the normal fluoride is 21.1 kg.-cal./gram-mole. The salt is tetragonal and the unit prism measures 5.67 Å. on a side and 6.81 Å. high. The unit cell contains four  $\text{KHF}_2$  groups (2). The salt is readily soluble in water to form acid solutions. Solubility of the anhydrous salt at various temperatures has been calculated (10):

Temp., °C.....	-7.6	-4.9	-2.9	0	10	20	45	60	80
Soly., g./100 g. water.....	19.7	11.1	5.3	24.5	30.1	39.2	61.3	78.4	114.0

Hydrofluoric acid increases the solubility of the salt in water. It is soluble in dilute ethyl alcohol but insoluble in absolute alcohol.

*Manufacture.* Potassium bifluoride is prepared commercially from potassium carbonate and hydrofluoric acid. Enough hydrofluoric acid is added to a solution of



the carbonate to provide a slight excess of acid over that necessary to form the bifluoride. The solution is then concentrated to 40–45°Bé. and allowed to crystallize. The crystals are dried and ground to make the commercial product.

The commercial salt contains 99.0%  $\text{KHF}_2$ . Small amounts of potassium fluosilicate, sulfate, and normal fluoride are usually present as impurities.

**Toxicology.** Potassium bifluoride is poisonous if taken internally, and, since it is an acid salt, it will cause skin burns similar to hydrofluoric acid if it comes in contact with the skin for any length of time. The molten salt has a decided tendency to split off hydrofluoric acid, and work with the material should be confined to hooded or ventilated areas.

**Uses.** Potassium bifluoride is used in the molten state or dissolved in anhydrous hydrogen fluoride as an electrolyte for the manufacture of fluorine (1,4,5,7,9). It has been proposed as a wood preservative to protect wood from destruction by fungi (11). The salt is the basis of most silver solder fluxes, and it is used in treating coal to prevent slagging of the ash in the boiler (12). Potassium bifluoride solutions frost glass, and the salt is used when a very fine frost is desired. In conjunction with boron trifluoride, it is used in alkylating benzene with olefins (13).

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G. C. WHITAKER

**Rare Earth Fluorides.** See *Rare earth metals and rare earth compounds*.

### Silicon Compounds.

#### Silicon Tetrafluoride.

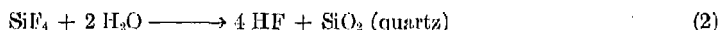
Silicon tetrafluoride (tetrafluorosilane),  $\text{SiF}_4$ , formula weight 104.06, is a colorless gas that fumes in moist air and has a sharp odor. It dissolves in water with chemical reaction. It is used principally as a source of fluosilicic acid and its salts. Minor catalytic and insecticidal applications have been reported. Silicon tetrafluoride was discovered by Scheele in 1771 in his work on the action of sulfuric acid on silica-containing fluorspar. Berzelius established its identity.

Aqueous solutions of silicon tetrafluoride are dealt with separately under "Fluosilicic acid" (p. 725).

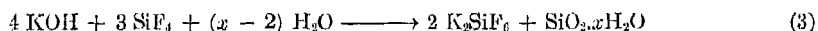
*Properties* (12,15). Silicon tetrafluoride has the following constants: m.p.,  $-90.2^{\circ}\text{C.}$  under a pressure of 1318 mm. (triple point); b.p.,  $-95.0^{\circ}\text{C.}$ ; vapor pressure (in mm.),  $\log p = 8.453 - 957.0/T$ ; subl. pressure (in mm.),  $\log p = 10.469 - 1352.8/T$ ; density of gas (in grams/liter),  $d = 4.64361 + 0.04688p$  (where  $p$  is in atm.); molar refractive index, 8.40; heat capacity,  $C_p^0$ , 18.2 cal./gram-mole/ $^{\circ}\text{C.}$ ; crit. temp.,  $-14.15 \pm 0.02^{\circ}\text{C.}$ ; crit. pressure,  $36.66 \pm 0.05$  atm.; heat of formation at  $25^{\circ}\text{C.}$ ,  $-370$  kg.-cal./gram-mole; heat of sublimation at  $177.7^{\circ}\text{K.}$  and 1 atm., 6.15 kg.-cal./gram-mole; heat of fusion at  $182.9^{\circ}\text{K.}$  and 1320 mm., 1.69 kg.-cal./gram-mole; heat of vaporization at  $182.9^{\circ}\text{K.}$  and 1320 mm., 4.46 kg.-cal./gram-mole; heat of dissociation, 232 kg.-cal./gram-mole. The solubility of silicon tetrafluoride, in weight per cent, in various solvents is: 32.8% in methanol, 36.4% in absolute ethyl alcohol, 38.1% in 95% ethyl alcohol, 28.2% in isopropyl alcohol, 23.4% in butyl alcohol, 26.2% in glycol, 5.7% in glycerol, 3.1% in acetone, and 1.1% in acetic acid.

Silicon tetrafluoride is said not to react with hydrogen (in sunlight), carbon, phosphorus, iodine, most other nonmetals, zinc, mercury, hydrogen sulfide, nitric acid, nitrogen tetroxide, nitrogen pentoxide, fused potassium chlorate, and anhydrous alkali carbonates and borates. Sodium and potassium, when heated, take fire in silicon tetrafluoride and produce a mixture of silicon, alkali fluoride, and alkali fluosilicate. Heated aluminum also reduces the compound to silicon. Iron and platinum are reported to form silicides.

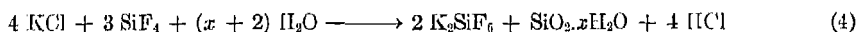
The behavior of silicon tetrafluoride with water (8) and bases is of technological importance in connection with its recovery from waste gases, notably from superphosphate fertilizer den gases. Reaction with water may follow two courses: equation (1) shows the reaction that takes place in liquid water, and equation (2), the reaction at high temperatures, for example, at red heat:



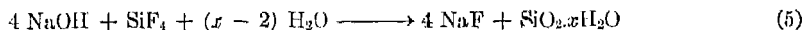
With dilute potassium hydroxide solution, silicon tetrafluoride first forms the insoluble fluosilicate and silicic acid (eq. 3):



Concentrated aqueous potassium chloride also precipitates the fluosilicate (eq. 4):

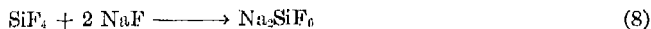


The alkalis and alkali carbonates, after forming the metal fluosilicate as in equation (3), will react further to produce the alkali fluoride and insoluble silicic acid (eq. 5), or, with excess alkali, soluble sodium silicate (eq. 6):



Aqueous ammonia forms ammonium fluoride and bifluoride (17). Gaseous ammonia reacts with silicon tetrafluoride to yield the volatile white solid  $\text{SiF}_4 \cdot 2\text{NH}_3$ . Calcium oxide becomes incandescent in silicon tetrafluoride, forming silica and calcium fluoride. The oxides of magnesium, aluminum, manganese, mercury, and iron react in a similar manner, but without ignition.

Reaction with hydrofluoric acid or solid sodium fluoride results in the formation of fluosilicic acid (eq. 7) or sodium fluosilicate (eq. 8), respectively:



Silicon tetrafluoride reacts with ethyl alcohol to form a strongly acid fluid containing ethyl orthosilicate and fluosilicic acid. It is said to form addition products with many organic compounds such as acetone and aromatic amines, and to react with Grignard reagents (5) to form the trialkyl- or triarylsilicyle fluorides, which are very much more stable than the corresponding chlorides.

*Manufacture.* Silicon tetrafluoride is not sold commercially. It may be prepared on a small scale by the action of concentrated sulfuric acid on a mixture of sand or glass and a fluoride such as fluorspar (1,16). The reaction of sulfuric acid with a mixture of sodium fluosilicate and ground silica is a very convenient method and is said to give a minimum of contamination (1). Other methods are reviewed by Mellor (10).

The most abundant source of silicon tetrafluoride, however, is the waste gas from superphosphate manufacture (7), from which it is recoverable as fluosilicic acid or as fluosilicates (see *Fertilizers*). The fluorine content of North American phosphate rocks varies between about 2.5 and 4.5%. In processing phosphate rock, about 25–30% of the fluorine is volatilized as hydrogen fluoride and silicon tetrafluoride, which, at present levels, is a potential source of about 35,000 tons of fluorine a year. Additional quantities of silicon tetrafluoride could be produced by the sulfuric acid treatment of low-grade (high-silica) fluorspar or recovered as by-product in phosphoric acid manufacture (19).

*Economic Aspects.* The production of silicon tetrafluoride from all sources far exceeds its utilization in the manufacture of fluosilicic acid and fluosilicates, and large amounts of this compound are therefore discarded. With the foreseeable depletion of high-grade fluorspar and the very rapid development of organic and inorganic fluorochemicals, it is probable that industry will turn to phosphate rock and low-grade fluorspar as sources of fluorine. Consequently, technological developments in the production of more useful fluorine compounds from silicon tetrafluoride may be expected. The major difficulty in realizing the fluorine values of silicon tetrafluoride appears to be in the production of silica-free products.

*Analysis.* Silicon tetrafluoride is generally absorbed in water and determined as fluosilicic acid. Trace amounts, for example in the effluent hydrocarbon gases from alkylation with hydrogen fluoride, are determined colorimetrically (2) by absorption in sodium bicarbonate and conversion to silicomolybdic acid. A special acidimetric method (14) has also been devised for the determination of silicon tetrafluoride in the presence of boron trifluoride, sulfur dioxide, and other gases.

*Health Hazards.* The toxicity of silicon tetrafluoride has not been evaluated. However, since the gas is both irritating and toxic, adequate ventilating and disposal systems should be provided wherever it is used or generated.

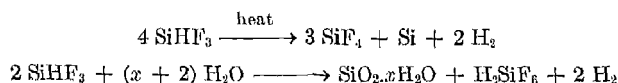
*Uses.* Silicon tetrafluoride is used chiefly for the manufacture of fluosilicic acid (18) (see p. 726). Smaller amounts have been converted to synthetic cryolite and other fluoaluminates (3). Its use as a catalyst (4,20), in catalyst manufacture (11,21), as a grain fumigant (9), and for the hardening of artificial stone, concrete, etc., has been reported.

### Other Fluorosilanes.

*Hexafluorodisilane* (disilicon hexafluoride),  $\text{Si}_2\text{F}_6$ , formula weight 170.12, is a colorless gas; m.p.,  $-18.5^\circ\text{C}$ . at 780 mm. pressure; subl. pt.,  $-19.1^\circ\text{C}$ .; density,

7.759 grams/liter at 0°C. It is prepared by the action of anhydrous zinc fluoride on hexachlorodisilane. Water immediately hydrolyzes it to silicooxalic acid, (SiOOH)<sub>2</sub>, silicic acid, and fluosilicic acid. Higher homologs are not known (13).

*Trifluorosilane* (silicofluoroform), SiHF<sub>3</sub>, formula weight 86.07, is a colorless combustible gas; m.p., -110°C.; b.p., -80.2°C. It is prepared by treating trichlorosilane (silicochloroform) with stannic fluoride or titanium tetrafluoride. Decomposition occurs upon heating or upon the addition of water:



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W. S. W. McCARTER AND W. A. BLUM

### Fluosilicic Acid.

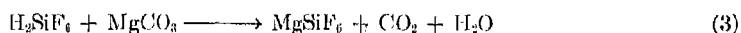
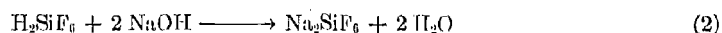
Fluosilicic acid of commerce (hexafluorosilicic acid, hydrofluosilicic acid, silico-fluoric acid) is a 30-35% aqueous solution of H<sub>2</sub>SiF<sub>6</sub>, formula weight 144.08. It is a colorless, fuming, corrosive liquid having a pungent odor and an irritating action on the skin. Fluosilicic acid is produced from silicon tetrafluoride and is used for the manufacture of inorganic and organic fluosilicates, in various electrolytic processes, in the ceramic industry as a hardening agent, as a preservative and hardening agent for certain building materials, and as a disinfectant.

*Properties.* Anhydrous fluosilicic acid is not known. Three solid hydrates, described as colorless fuming crystals, have been reported. Aqueous solutions alone are of industrial importance. Their boiling points increase with increasing acid content; for pure acid of a commercial strength (30.2% H<sub>2</sub>SiF<sub>6</sub>), the boiling point at 720 mm. pressure is 108.5°C. The densities at 17.5°C. for various concentrations are:

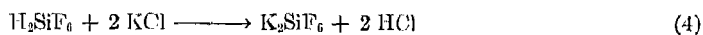
H <sub>2</sub> SiF <sub>6</sub> , %.....	6	14	22	30	34	61
d <sub>4</sub> <sup>17.5</sup> .....	1.0491	1.1190	1.1941	1.2742	1.3126	1.4634 <sup>26</sup>

The heat of formation from silicon tetrafluoride and water is given as 67 kg.-cal./gram-mole, from silicon tetrafluoride and hydrogen fluoride as 33.9 kg.-cal./gram-mole, from silicon dioxide and hydrogen fluoride as 8.95 kg.-cal./gram-mole, and of  $\text{H}_2\text{SiF}_6 \cdot \text{H}_2\text{O}$  from the elements and water as 374.3 kg.-cal./gram-mole. Fluosilicic acid is said to evaporate at temperatures as low as 40°C. without residue. In the vapor phase, fluosilicic acid exists as  $\text{SiF}_4 + 2 \text{HF}$ . A 13.3% solution of fluosilicic acid distills without decomposition, that is, the vapor contains silicon tetrafluoride and hydrogen fluoride in the ratio of 1:2. The vapor from a boiling acid of lower concentration will be richer in hydrogen fluoride than is indicated by that ratio, whereas the vapor from an acid of higher concentration will be richer in silicon tetrafluoride with the result that the distilland will contain free hydrofluoric acid. The acid can be concentrated, however, to about 61% by distillation at room temperature under reduced pressure (6). Liquid-vapor equilibria in the system  $\text{H}_2\text{SiF}_6\text{-HF-H}_2\text{O}$  have been determined (11).

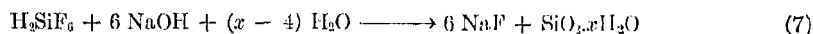
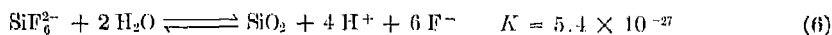
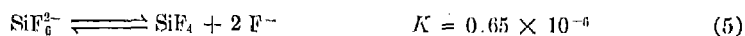
Fluosilicic acid reacts as a dibasic acid with certain metals, metal oxides, and dilute solutions of hydroxides and carbonates, forming fluosilicates (eq. 2 and 3):



The sparingly soluble fluosilicates of barium, potassium, and sodium are precipitated when a soluble salt of one of those metals is added to fluosilicic acid (eq. 4):

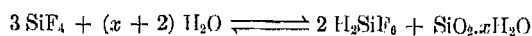


Other equilibria (12) exist in fluosilicic acid solutions (eq. 5 and 6), and by virtue of these it is possible to convert fluosilicic acid, or a fluosilicate, into fluorides by the use of excess base, usually at an elevated temperature (eq. 7):



Ammonia may also react to form either the fluosilicate or the fluoride. By a similar mechanism, fluosilicic acid converts hydrated alumina into aluminum fluoride, and a mixture of alumina and alkali into a fluoaluminate such as synthetic cryolite (2,16). Finely divided quartz is soluble in fluosilicic acid. Boric acid and fluosilicic acid produce a solution of fluoboric acid and a precipitate of silicic acid. Hydrazine and hydroxylamine form fluosilicates. Alkyl, aryl, and heterocyclic amines also form fluosilicates, some of which are said to be useful as wood preservatives, disinfectants, and antiseptics (7,18,19).

*Manufacture.* Fluosilicic acid is formed when silicon tetrafluoride dissolves in water (21):



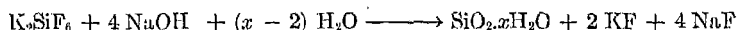
When this acid is produced in conjunction with superphosphate manufacture (see *Fertilizers*), the fertilizer den gases, containing low concentrations of silicon tetrafluoride and water vapor, are drawn through fans to a tower, equipped with trays, where they are absorbed in recirculating dilute fluosilicic acid at about 160°F. By

using a high recirculation rate, the by-product silica is washed down and collected in the conical bottom of the tower. When the recirculating acid reaches strength, the system is discharged to the filters, which remove the silica. The den-gas ducts, the fans, the absorbing tower, and the vacuum filters are lined with neoprene. The acid-recirculating pump is of Monel. Storage tanks for cold acid are rubber-lined. The maximum concentration attainable by the absorption method is 25–30%. This acid will contain an appreciable amount of free silica.

Fluosilicic acid is also made by dissolving silica (sand) in aqueous hydrofluoric acid of suitable concentration, keeping the silica in excess to insure that the product is free of hydrogen fluoride. Silica is not formed in this reaction. Rubber-lined tanks, with agitators, are used. This is a considerably more expensive method of manufacture, and it is used when higher concentrations or a product free of colloidal silica is desired.

*Grades.* Technical (30 and 35%) and analytical (30%) grades are marketed. The technical grade is shipped in 500-lb. or 160-lb. barrels or in 125-lb. rubber drums (I.C.C.-43A). It is classed as a corrosive liquid by the I.C.C. and shipped under a white acid label, manifested as "hydrofluosilicic acid." Current prices (February 1950) are about 5¢ per pound for technical grade in barrels, and about \$1.40 per pound for the analytical grade in 1-lb. bottles.

*Analysis.* While the method of analysis of fluosilicic acid solutions is influenced to a certain extent by the nature of the other substances present, the double-titration method may be considered basic. Potassium fluosilicate is first precipitated at about 0°C. by the addition of potassium chloride solution and alcohol; the hydrochloric acid liberated (see eq. 4, p. 726) is then titrated in the cold with standard alkali, using methyl orange as indicator. If other acids are present, this titration will, of course, give high results. As a check on this titration, the solution is heated to 80–95°C. and titrated with standard alkali, using phenolphthalein as indicator:



The second titer should be twice the first if no other acids were present. Jacobson (6) recommends a correction factor of 0.6% (negative) in the second titration to allow for consumption of alkali by silicic acid. Free silica may be estimated from the difference between the first acidity titrations with and without the addition of neutral fluoride.

*Health Hazards.* In contact with the skin, fluosilicic acid and some of its salts cause an irritation followed by ulceration unless normal protective and sanitary measures are observed. Fluosilicic acid and sodium fluosilicate are highly toxic, and fatalities resulting from the ingestion of proprietary preparations containing these compounds have been recorded. The symptoms of fluosilicate poisoning resemble those of fluoride poisoning. The inhalation of dusts containing fluosilicates is also capable of causing pulmonary irritation and even death.

*Uses.* Fluosilicic acid is used for making fluosilicates and fluorides; as an ingredient of disinfecting solutions in general, but particularly for brass and copper equipment in distilleries and breweries; as an ingredient in impregnants used to preserve wood and to harden and waterproof masonry, cement, plaster, etc.; as an agent for increasing the hardness of china, porcelain, and pottery; as an ingredient in concrete flooring compositions; in the preliminary treatment of skins and hides; in certain electrochemical operations such as the electrolytic refining of lead and the electroplating of chromium; in technical paints; for treating glass surfaces to reduce reflec-

TABLE I. Physical Properties of Some Inorganic Fluosilicates.

Salt	Formula wt.	Appearance	Sp.gr.	Refractive index		Soly., g./100 ml. water at °C.	Soly. in other solvents
				$\omega$	$\epsilon$		
$\text{Al}_2(\text{SiF}_6)_3 \cdot 9\text{H}_2\text{O}$	642.3	Hexagonal prisms	—	—	—	v.s. cold	—
$(\text{NH}_4)_2\text{SiF}_6$	178.14	Colorless, cubic	2.011	1.3696	—	18.53 <sup>17.5</sup> ; 55.5 <sup>100</sup>	s. alc.; i. acetone
$\text{BaSiF}_6$	279.42	Colorless, hexagonal	2.152	—	—	—	—
$\text{CaSiF}_6$	182.14	Colorless, rhombic needles	4.279	—	—	0.025 <sup>25</sup> ; 0.044 <sup>78</sup>	sl.s. acids; i. alc.
$\text{Cs}_2\text{SiF}_6$	407.88	White powder, tetragonal	2.662	—	—	10.58 <sup>25</sup> (dec.)	s. HF, HCl, alc.
$\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$	309.10	White, cubic or octahedral	3.375	—	—	0.60 <sup>17</sup>	i. alc.
$\text{Cu}_2\text{SiF}_6$	269.20	Pink, trigonal	2.113	1.3817	1.3872	118.1 <sup>21.5</sup>	—
$\text{Cu}_2\text{SiF}_6$	269.20	Red powder	—	—	—	i.; dec. 100 °C.	—
$\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$	313.73	Blue, rhombic, efflorescent	2.207	1.4092	1.4080	233 <sup>17</sup>	sl.s. alc.
$\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$	306.00	Pale blue-green, trigonal	1.961	1.3638	1.3848	128.2 <sup>2</sup>	i. alc., acetone
$\text{PbSiF}_6 \cdot 4\text{H}_2\text{O}$	421.33	Colorless, monoclinic, efflorescent	—	—	—	68.97 <sup>20</sup> °; 81.06 <sup>30</sup> °	—
$\text{Li}_2\text{SiF}_6 \cdot 2\text{H}_2\text{O}$	191.97	White, monoclinic	2.33	1.300	1.296	52.6 (cold); 73 <sup>17</sup>	s. alc.; i. ether, acetone
$\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$	274.48	White, trigonal	1.788	1.3439	1.3602	23.53 <sup>20</sup> °; 30.74 <sup>68</sup> °	i. alc.
$\text{MnSiF}_6 \cdot 6\text{H}_2\text{O}$	305.09	Rose, hexagonal prisms	1.858	1.3570	1.3742	140.8 <sup>11.5</sup>	s. alc.
$\text{Hg}_2\text{SiF}_6 \cdot 2\text{H}_2\text{O}$	579.31	Colorless, prisms	—	—	—	sl.s. cold	i. HCl
$\text{HgSiF}_6 \cdot 6\text{H}_2\text{O}$	450.77	Colorless, rhombohedral, deliquescent	—	—	—	v.s. cold (dec.)	—
$\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$	308.85	Green, trigonal	2.134	1.3910	1.4066	v.s. cold	—
$\text{K}_2\text{SiF}_6$	220.25	Colorless, cubic	2.746	1.339	—	0.177 <sup>25</sup> ; 0.462 <sup>78</sup>	s. HCl; i. alc., $\text{NH}_3$
$\text{K}_2\text{SiF}_6$	220.25	Colorless, hexagonal	3.081	—	—	—	—
$\text{Rb}_2\text{SiF}_6$	313.02	Opalescent, cubic, or hexagonal	3.338	—	—	0.160 <sup>20</sup> ; 1.360 <sup>100</sup>	s. acids; i. alc.
$\text{Ag}_2\text{SiF}_6 \cdot 4\text{H}_2\text{O}$	429.88	Colorless, octahedral, deliquescent	—	—	—	v.s. cold	s. alc.
$\text{Na}_2\text{SiF}_6$	188.05	Colorless, hexagonal	2.755	1.312	1.309	0.762 <sup>25</sup> ; 1.822 <sup>78</sup>	i. alc.
$\text{SrSiF}_6 \cdot 2\text{H}_2\text{O}$	265.72	White, monoclinic	2.99	—	—	3.22 <sup>15</sup> ; v.s. hot	s. HCl; i. alc.
$\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$	315.54	Colorless, hexagonal prisms	2.104	1.3824	1.3956	35.16 <sup>20</sup> °; 40.95 <sup>80</sup> °	s. methanol

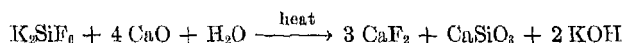
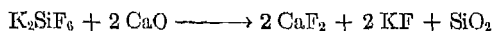
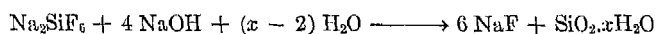
° As anhydrous salt.

tion; and, in conjunction with mercuric compounds, as a catalyst for reactions between acetylene and phenols, amines, etc.

### Metal Fluosilicates

The metal fluosilicates (silicofluorides) do not occur naturally in significant amounts; the sodium, potassium, and ammonium salts have been reported in certain volcanic fumaroles. The fluosilicates are prepared by treating fluosilicic acid with a suitable precipitating or neutralizing agent (15). The barium, potassium, rubidium, cesium, and sodium salts are sparingly soluble in water and, like the ammonium salt, occur only as anhydrous salts. The difficultly soluble fluosilicates may be "solubilized" by treatment with a solution containing less than the chemical equivalent of a salt of a metal that forms a soluble fluosilicate, for example, magnesium sulfate, a weak base such as aniline, and a polyhydric alcohol such as glycerol (17). Aqueous solutions of soluble fluosilicates, upon treatment with benzidine or tolidine in hot alcohol or acetone, form insoluble complex salts of the type  $[\text{Cu}(\text{NH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NH}_2)_2]\text{SiF}_6$  (13). Pyridine complexes have also been described (14). The physical properties of the more important fluosilicates are summarized in Table I.

The fluosilicates, in aqueous mediums, are converted to metal fluorides and silicic acid (or silicates) by the action of excess oxide, hydroxide, or carbonate; for example:



Such reactions frequently complicate the preparation of pure fluosilicates; consequently, concentrations and temperatures must be carefully controlled.

The metal fluosilicates are decomposed thermally into metal fluorides and silicon tetrafluoride (1,5). The barium, potassium, and sodium salts are most stable and do not begin to decompose in that fashion much below a dull red heat. The heavy-metal fluosilicates are least stable; some decompose at temperatures as low as 100°C.

The metal fluosilicates are reduced to elemental silicon by electrolysis of the molten salt or by treatment with an element more electropositive than silicon.

*Sodium fluosilicate* (4) is manufactured by adding sodium chloride or soda ash to 25% fluosilicic acid in rubber-lined tanks equipped with suitable agitators, centrifuging the resulting slurry, and drying the solid product in conventional equipment. It is used as an opacifying agent in the manufacture of vitreous enamels and opalescent glass, as a coagulant for latex, to treat hides and skins to facilitate tanning, in making zirconia pigments, and in the extraction of beryllium (see Vol. 2, p. 494). As an insecticide, sodium fluosilicate is more toxic than sodium fluoride or the arsenicals, yet it is less poisonous to the higher animals.

*Ammonium fluosilicate* is produced by neutralizing fluosilicic acid with gaseous or aqueous ammonia under controlled conditions in neoprene- or lead-lined reactors, concentrating the resulting solution in a vacuum crystallizer, recovering the crystallized salt in a rubber-lined centrifuge, and drying the product. Ammonium fluosilicate is used as a laundry sour and in the sand-mold casting of magnesium. It has also been suggested for use as a reagent to extract potassium from greensand and other minerals (18).



*Zinc fluosilicate* is produced from zinc carbonate and fluosilicic acid in a neoprene-lined vacuum crystallizer equipped with copper steam coils. The zinc salt has been used as a laundry sour, to preserve wood, as an additive to strengthen plaster, and to precipitate potash from sugar liquors and other solutions.

*Calcium fluosilicate* is made from the oxide, carbonate, or chloride. It is used in the ceramic industry as an opacifying agent, to harden and waterproof various materials of construction, and as an insecticide.

*Copper fluosilicate*, usually prepared from basic copper carbonate, is used for dyeing and hardening marble, as an insecticide and fungicide (especially for grape vines), and as an activating agent in certain flotation processes.

*Silver fluosilicate* is an antiseptic, and an activating agent in flotation processes.

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W. S. W. McCARTER AND W. A. BLUM

### Silver Compounds.

**Silver fluoride**,  $\text{AgF}$ , formula weight 126.88, is variously reported as a yellow-to-brown crystalline (cubic) solid; m.p.  $435^\circ\text{C}$ .; b.p. about  $1150^\circ\text{C}$ .; sp.gr. 5.852. Its solubility in water has been reported as 172 grams/100 grams water at  $20^\circ\text{C}$ . and 205 grams at  $108^\circ\text{C}$ . Silver fluoride is deliquescent and light-sensitive. To avoid the difficult wet method of preparation from hydrofluoric acid and silver carbonate, silver fluoride may be made on a moderate scale by the reduction of silver difluoride with hydrogen. Silver fluoride is a powerful antiseptic and has been used as such in medicine.

**Silver difluoride**,  $\text{AgF}_2$ , formula weight 145.88, is a brown free-flowing powder; m.p.  $690^\circ\text{C}$ .; sp.gr. 4.57-4.78. It is readily hydrolyzed by atmospheric moisture. It is prepared by passing fluorine, diluted with nitrogen, over silver chloride, while the temperature is gradually increased to about  $200^\circ\text{C}$ . Silver difluoride is used as a fluorine carrier in the production of fluorocarbons.

A silver trifluoride,  $\text{AgF}_3$ , formula weight 164.88, has also been reported; m.p.,  $-5.9^\circ\text{C}$ .; b.p.,  $57.1^\circ\text{C}$ .

F. D. LOOMIS

### Sodium Compounds.

**Sodium fluoride**,  $\text{NaF}$ , formula weight 42.00, is a white crystalline powder (tetragonal or cubic); m.p.  $992^\circ\text{C}$ .; b.p.  $1704^\circ\text{C}$ .; sp.gr. 2.79;  $n_D$  1.3258; approximate solubility, 4 grams/100 grams water at  $0^\circ\text{C}$ . and 5 grams at  $100^\circ\text{C}$ . Sodium fluoride is made commercially by treating soda ash with aqueous hydrofluoric acid in a lead reactor, carefully controlling the pH to obtain the desired crystal size. The sodium fluoride is then dewatered, dried, and pulverized. Sodium fluoride is used in rimming steel, in soldering compositions and metallurgical fluxes, for pickling stainless steel, as an insecticide, as a wood preservative, for the fluoridation of water, as an opacifier in enamel manufacture, as an anthelmintic, in antifermentative and antiseptic compositions, in the manufacture of coated paper, and in frosting glass. Sodium fluoride is marketed as technical grades containing 90% and 95%  $\text{NaF}$ . Both grades are available in light (37 cu.in./lb.) and heavy (23 cu.in./lb.) forms. Sodium fluoride sold for insecticidal use must be colored blue. There are no shipping regulations.

F. D. LOOMIS

**Sodium bifluoride** (sodium hydrogen fluoride, sodium acid fluoride),  $\text{NaHF}_2$  or  $\text{NaF}\cdot\text{HF}$ , formula weight 62.005, is a white free-flowing powder, which is used chiefly as a laundry sour. Sodium bifluoride was first reported around 1820 by Berzelius, who synthesized it by dissolving the normal fluoride,  $\text{NaF}$ , in hydrofluoric acid or acetic acid and crystallizing the acid salt from the solution.

*Properties.* Sodium bifluoride is a white crystalline (rhombic or trigonal) solid. The finely divided commercial product has a bulk density of 60–70 lb./cu.ft. Other reported physical properties are as follows:  $d_4^{20}$  (satd. soln.), 1.033; heat of formation at  $18^\circ\text{C}$ ., 216.75 kg.-cal./gram-mole; heat of formation from hydrogen fluoride and sodium fluoride, 17.10 kg.-cal./gram-mole; heat of solution (in 400 moles  $\text{H}_2\text{O}$ ) at  $12^\circ\text{C}$ ., 6.2 kg.-cal./gram-mole; soly., 3.25 grams/100 ml. soln. at  $20^\circ\text{C}$ ., 7.50 grams at  $90^\circ\text{C}$ . Sodium bifluoride is decomposed by heat to normal fluoride and hydrofluoric acid. The rate of decomposition does not become appreciable until the salt reaches the temperature of 160–180°C.

*Manufacture.* Sodium bifluoride is made by the reaction of hydrofluoric acid or hydrogen fluoride with soda ash, caustic soda, or salt. The acid is usually a weak acid from a hydrofluoric acid plant and contains as impurities sulfuric acid and fluosilicic acid. In combining the reactants, an adequate concentration of excess acid is maintained in order to crystallize the bifluoride. The slurry of bifluoride from the crystallizer is centrifuged, and the dewatered crystals are then dried, screened, and packaged. A modification of the above procedure has been used wherein the centrifuge and dryer are replaced by a spray dryer.

In practice, the heat of reaction brings the operating temperature to 90–100°C. unless cooling is applied. This temperature poses a problem in so far as materials of construction are concerned. Tanks used as reactors have been constructed of wood or steel with rubber, carbon brick, or lead lining. Process piping consists of rubber hose

with pinch valves or rubber-lined diaphragm valves. Metals such as acid-resisting bronze, Monel, copper, and the stainless steels have been utilized for parts of the process equipment where the use of rubber, plastic, or carbon brick is not feasible. However, the various operating conditions such as temperature, degree of aeration, velocity, impurities, and acid content of the liquor must be taken into consideration in choosing the most suitable material of construction, and no general recommendations can be made.

Sodium bifluoride is packaged in fiber drums containing 125 or 375 lb. net. There are no I.C.C. shipping regulations.

*Analysis.* Sodium bifluoride is produced commercially as a technical grade, the purity or composition of which depends upon the raw materials used. Materials commonly found in commercial sodium bifluoride, together with the amounts normally encountered, are:  $\text{NaHF}_2$ , 90–98%;  $\text{Na}_2\text{SiF}_6$ , 1–5%;  $\text{Na}_2\text{SO}_4$ , 0–3%;  $\text{NaF}$ , 0–4%;  $\text{NaCl}$ , 0–6%;  $\text{FeF}_3$ , 0.0–0.04%. Testing of sodium bifluoride is accomplished by determining its acid value (or, in the case of the laundry industry, its souring value) by titrating against a standard base. This involves both a hot and a cold titration to differentiate between bifluoride and fluosilicate (see "Hydrogen fluoride," p. 706).

*Toxicology.* Sodium bifluoride is poisonous when taken internally. Prolonged breathing of the dust must be avoided. Upon contact with the skin, the salt hydrolyzes to sodium fluoride and hydrofluoric acid; this contact should be minimized to preclude skin irritation and typical acid fluoride burns.

*Uses.* The principal use of sodium bifluoride is as a sour in laundry operations to neutralize the excess alkali present and to remove discoloration due to iron (see *Laundering*). It is particularly useful for this application, inasmuch as textile fabrics are not attacked by the sodium bifluoride solution, nor is there any deposit left in the cloth that would result in an objectionable "feel." Sodium bifluoride is also used for cleaning the outside of masonry buildings, for etching and frosting glass, and for removing iron stains. It is a powerful antiseptic and has been used to treat anthrax-infested hides. It has also been used as a preservative, for example, for anatomical specimens.

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J. E. DODGEN

### Sulfur Compounds.

#### Sulfur Fluorides.

Five fluorides of sulfur have been reported in the literature (1,7,10). The identity and characteristics of the two highest members of the series have been definitely established. Although the two lowest members of the series have been identified, there is reason to believe they were never isolated in pure form, and the reported properties of these compounds are consequently open to some question. The stability of these compounds increases as the ratio of fluorine to sulfur increases. With the exception of the hexafluoride,  $\text{SF}_6$ , no commercial uses have been developed for these compounds in spite of their unusual properties.

*Sulfur monofluoride* (disulfur difluoride),  $S_2F_2$ , formula weight 102.12, is described as a colorless toxic gas that fumes in air and has a disagreeable odor. The following constants have been reported: m.p.,  $-105.5^\circ\text{C}.$ ; b.p.,  $-99^\circ\text{C}.$ ;  $d_4^{+100}$  (liquid), 1.5. Sulfur monofluoride hydrolyzes readily in moist air and in water to yield sulfur, sulfur dioxide, and hydrogen fluoride. Although the monofluoride is said not to react with iron, steel, tin, or platinum, it attacks glass and silica, even at low temperatures, yielding sulfur dioxide, silicon tetrafluoride, and thionyl fluoride,  $SOF_2$ . Sulfur monofluoride was first prepared by heating a mixture of sulfur and silver fluoride (2).

*Sulfur difluoride*,  $SF_2$ , formula weight 70.07, the least known of the series, is probably formed by the thermal decomposition of the monofluoride (11). It has not been prepared in pure condition and is probably very unstable.

*Sulfur tetrafluoride*,  $SF_4$ , formula weight 108.06, is described as a colorless gas with an irritating odor. It can be condensed to a liquid; f.p.,  $-124^\circ\text{C}.$ ; b.p.,  $-40^\circ\text{C}.$  It does not attack glass but is hydrolyzed by water and by alkali solutions, yielding sulfites and fluorides. The original preparation from cobaltic fluoride and sulfur at room temperature (4) was later shown to yield not pure tetrafluoride but a mixture of all the sulfur fluorides. The compound may be purified by shaking with mercury to remove the mono- and difluorides and by fractional distillation to remove the hexafluoride (1).

*Sulfur pentafluoride* (disulfur decafluoride),  $S_2F_{10}$ , formula weight 254.12, is a highly toxic colorless liquid; f.p.,  $-92^\circ\text{C}.$ ; b.p.,  $29^\circ\text{C}.$ ; vapor pressure (in mm.),  $\log p = 7.95 - 1530/T$ ;  $d_4^0$ , 2.08; surface tension, 13.9 dynes/cm.; Trouton constant, 23. Its increased stability, as compared with the lower fluorides, is demonstrated by the fact that this compound is not readily hydrolyzed by water or dilute caustic and does not attack glass or metals at low temperature. It is decomposed by fused caustic or by heat and reacts with heated metals to form sulfides. Disulfur decafluoride is formed in low yields when sulfur reacts with fluorine (3).

*Sulfur hexafluoride*,  $SF_6$ , formula weight 146.06, is a colorless, odorless, nontoxic gas that solidifies without liquefaction on cooling; m.p.,  $-50.8^\circ\text{C}.$  under pressure; sublimation temp.,  $-63.7^\circ\text{C}.$ ; sublimation pressure (in mm.),  $\log p = 8.7648 - 1231.3/T$ ; sp.gr., of gas at  $20^\circ\text{C}.$ , 753.5 mm., 5.106 g./l., of liquid at  $-50^\circ\text{C}.$ , 1.91, of solid at  $-50^\circ\text{C}.$ , 2.51;  $n_D^{20}$ , 1.000783; surface tension, 11.63 dynes/cm. at  $-50^\circ\text{C}.$ , 8.02 at  $-20^\circ\text{C}.$ ; heat capacity,  $C_p$ , 27.85 cal./gram-mole/ $^\circ\text{C}.$  at  $210^\circ\text{K}.$ , 44 at  $220^\circ\text{K}.$ , 28.56 at  $230^\circ\text{K}.$ ; Trouton constant, 22; other thermodynamic properties are given in Table I; critical properties and vapor pressure are given in Table II. The liquid

TABLE I. Thermodynamic Properties of Sulfur Hexafluoride.

Change	Temp., $^\circ\text{C}.$	Heat content, $\Delta H$ , kg.-cal./gram-mole	Entropy, $\Delta S$ , cal./gram-mole/ $^\circ\text{K}.$
Transition.....	-178.9	0.384	4.07
Fusion.....	-50.7	1.20	5.40
Sublimation.....	-63.7	5.46	26.04
Vaporization.....	-50.7	4.08	18.34

Source: reference (8).

stored in steel cylinders shows a pressure of 330 p.s.i.g. at  $25^\circ\text{C}.$  Sulfur hexafluoride has a high dielectric strength and is stable in the silent electrical discharge. It is receiving consideration as an insulating gas in high-voltage equipment.

TABLE II. Critical Properties and Vapor Pressure of Sulfur Hexafluoride.

Source of data	Crit. temp., °C.	Crit. pressure, p.s.i.a.	Crit. density, g./ml.	Vapor pressure of liquid, p.s.i.a.
Pennsylvania Salt Mfg. Co. (7a) . . . . .	45.5	540	0.727	$\log p^a = 5.595 - 907.98/T$
General Chemical Division . . . . .	45.6	540	0.755	$\log p = 5.524 - 889.85/T$

<sup>a</sup> Vapor pressure for the range -50 to 40°C.

Sulfur hexafluoride is practically insoluble in water. It is noncorrosive and has been compared to nitrogen with regard to its chemical inertness. It will react with hydrogen, metals, and glass only at a red heat. Sulfur hexafluoride is readily prepared by the direct combination of sulfur and gaseous fluorine (9), and it is purified by thermal treatment at 400°C. and alkali scrubbing to decompose and remove the lower fluorides, followed by drying over solid caustic.

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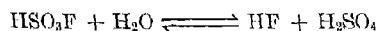
### Fluosulfonic Acid.

Fluosulfonic acid (fluorosulfonic acid),  $\text{FSO}_3\text{H}$  or  $\text{HSO}_3\text{F}$ , formula weight 100.07, is a mobile, almost colorless liquid that fumes strongly in moist air and has a sharp, irritating odor. This compound is the fluorine analog of chlorosulfonic acid (*q.v.*), which it resembles in certain respects; however, fluosulfonic acid and certain fluosulfonates (both inorganic and organic) are said to be more stable, particularly toward water, than the corresponding chlorine compounds. Fluosulfonic acid was first prepared, identified, and characterized by Thorpe and Kirman. This acid has been used as a catalyst, and as a reagent for the production of increasingly important organic fluorine compounds.

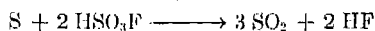
*Properties.* Fluosulfonic acid has the following constants: m.p.,  $-87.3^\circ\text{C}.$ ; b.p.,  $162.6^\circ\text{C}.$ ;  $b_{120}$ ,  $110^\circ\text{C}.$ ;  $b_{10}$ ,  $77^\circ\text{C}.$ ;  $d_4^{18}$ , 1.740.

Thorpe and Kirman were of the opinion that fluosulfonic acid could not be distilled without some decomposition into sulfuric acid and sulfuryl fluoride,  $\text{SO}_2\text{F}_2$ , but the later work of Ruff (9) showed that the acid is extremely stable to heat and does not decompose below  $900^\circ\text{C}.$  Vapor-phase dissociation into hydrogen fluoride and sulfur trioxide probably occurs. The solution of fluosulfonic acid in water is attended by a

violent release of energy. Unlike chlorosulfonic acid, however, fluosulfonic acid is neither instantaneously nor completely hydrolyzed (14), especially at lower temperatures:



The pure acid does not react in the cold with sulfur, selenium, tellurium, carbon, silver, copper, zinc, iron, chromium, or manganese but slowly dissolves mercury and tin (7). At higher temperatures, lead, mercury, tin, and sulfur react rapidly; for example:



Precipitated silicic acid reacts vigorously with fluosulfonic acid, with the evolution of silicon tetrafluoride (9). Glass, on the other hand, is not attacked by the acid in the absence of moisture (7). Alkali metal chlorides are readily converted by fluosulfonic acid into fluosulfonates, with the liberation of hydrogen chloride (9). Fluosulfonic acid reacts with boric acid in sulfuric acid solution or in crystal form to give boron trifluoride (24).

Depending upon reaction conditions and the proportions of reagents used, fluosulfonic acid will convert benzene into benzenesulfonic acid (7, 10), phenyl sulfone (10), or benzenesulfonyl fluoride (11). Aromatic compounds in general are converted into the corresponding arylsulfonyl fluorides. While ammonium fluosulfonate is the more common reagent, fluosulfonic acid may be used for the preparation of diazonium fluosulfonates (21), which are said to be insensitive to friction and percussion, but which, on heating, are decomposed to aryl fluosulfonates (5, 19). Glacial acetic, propionic, phenylacetic, monochloroacetic, and dichloroacetic acids form the corresponding acyl fluorides upon treatment with fluosulfonic acid (13). Ethyl fluosulfonate is produced by the interaction of ethylene (18), ethyl alcohol, or ethyl ether (7) and fluosulfonic acid. Cellulose dissolves in fluosulfonic acid to form a clear, brown, viscous liquid, which is possibly a mixture of tetra- and some trifluosulfonyl ester (8).

*Preparation and Manufacture.* Fluosulfonic acid was first prepared by distilling a slight excess of anhydrous hydrogen fluoride into a quantity of strongly chilled liquid sulfur trioxide, in platinum, and then removing the excess hydrogen fluoride by blowing with carbon dioxide at 25–30°C. The preparations of fluosulfonic acid from potassium bifluoride (7) or ammonium fluoride (12) and fuming sulfuric acid, and from ammonium fluosulfonate and 99% sulfuric acid (7) have been reported. The reaction of chlorosulfonic acid with ammonium fluoride (or an alkali or alkaline earth fluoride) at 40–150°C. has also been suggested (22) as a means of preparing this acid.

Commercially, fluosulfonic acid is made by treating liquid or gaseous hydrogen fluoride with liquid or gaseous sulfur trioxide (16) in a suitable reaction chamber under anhydrous conditions. Both iron and aluminum (or high-aluminum alloy) have been suggested for reactor construction. The most recently published process improvement (29) utilizes the product as solvent for the reaction of additional quantities of hydrogen fluoride and sulfur trioxide in exact stoichiometric proportions. A technical grade, containing a minimum of 96%  $\text{HSO}_3\text{F}$ , is marketed.

*Analysis.* The analysis of fluosulfonic acid (7) involves transferring a weighed sample in a stoppered container to a flask containing a quantity of water, and, after stoppering the flask, allowing the sample to react with the water. Barium sulfate is then precipitated by the addition of hydrochloric acid and barium chloride. The barium sulfate will be contaminated with barium fluoride, which can be determined

and corrected for, after drying and weighing the precipitate, by fuming off with concentrated sulfuric acid.

The fluosulfonate ion forms only one known sparingly soluble salt, the nitron salt (4,13) (solubility, 0.0318 gram/100 ml. water).

*Handling.* The immediate action of fluosulfonic acid on the skin is similar to that of concentrated sulfuric acid. In addition, the severe penetrating action and delayed attack characteristic of acid fluorides may be expected if the acid remains on the skin. Precautions and first-aid measures generally observed in handling strong sulfuric and hydrofluoric acids are applicable to fluosulfonic acid. Small containers should be chilled and opened with care.

In the laboratory, fluosulfonic acid may be handled in glass if water vapor is excluded; otherwise, platinum should be used. Rubber, cork, wood, and lead are rapidly attacked by fluosulfonic acid. For larger-scale equipment, iron or steel (not stainless steel) may be used with but little contamination.

Fluosulfonic acid is shipped as a corrosive liquid, under a white label, in steel tank cars, and in 55- and 20-gal. steel drums. Small quantities are packaged in glass.

*Uses.* Fluosulfonic acid serves as a catalyst in the alkylation of isoparaffins (17,23) and aromatic compounds (27), and in the polymerization of monoolefins (26) and rosin (25). As a reagent, it has been employed in the preparation of boron trifluoride (24), alkyl fluosulfonates (7,18), arylsulfonyl fluorides (11) (which are useful as lubricating-oil additives and in cutting oils), acyl fluorides (13), sulfamic acids (13), and the stable diazonium fluosulfonates (21). The use of fluosulfonic acid for ring closure and subsequent oxidation, as in the preparation of thioindigoid dyes from arylthioglycolic (arylmercaptoacetic) acids, has been demonstrated (20). Among its other uses are the removal of small amounts of organic fluorides from petroleum alkylate made by the hydrogen fluoride process (28), the removal of hydrogen fluoride from exhaust process gases (30), the preservation of wood, and as a constituent of baths used for electropolishing certain metals.

### Inorganic Salts

The physical properties of some of the more important fluosulfonates are summarized in Table I.

TABLE I. Physical Properties of Some Inorganic Fluosulfonates.

Salt	Formula wt.	Appearance	M.p., °C.	Soly., g./100 ml. water	Soly. in other solvents
NH <sub>4</sub> SO <sub>3</sub> F	117.10	Long colorless needles	245	s.	sl.s. alc.; v.s. methanol
CsSO <sub>3</sub> F	231.98	Colorless rhombic	292	2.23	—
LiSO <sub>3</sub> F·3H <sub>2</sub> O	160.06	Long shiny needles	60–61	v.s.	{ v.s. alc., ether, acetone, amyl alc., ethyl acetate; i. ligroin
LiSO <sub>3</sub> F	106.01	White powder	360	v.s.	
KSO <sub>3</sub> F	138.16	Short white prisms	311	6.9	sl.s. methanol
RbSO <sub>3</sub> F	184.56	Colorless needles	304	s.	sl.s. methanol
NaSO <sub>3</sub> F	122.07	Shiny leaflets, hygroscopic	—	s.	s. alc., acetone; i. ether

*Ammonium fluosulfonate* is produced from ammonium fluoride by reaction with sulfur trioxide, oleum, or potassium pyrosulfate (12). Solutions of ammonium fluosulfonate show no evidence of hydrolysis; in fact, this salt can be recrystallized from

hot water. Ammonium fluosulfonate absorbs anhydrous ammonia to form a series of liquid amines that contain from 2.5 to 6 moles of ammonia per mole of salt, depending upon the temperature (13).

*Sodium fluosulfonate* may be prepared by the action of fluosulfonic acid on powdered ignited sodium chloride (9) or of sulfur trioxide on sodium fluoride (12); in the latter case, the fluosulfonate is separated from unreacted fluoride by solution in and recrystallization from alcohol. Sodium fluosulfonate solutions are also neutral to litmus and give no evidence of hydrolysis. At a red heat, sodium fluosulfonate decomposes into sodium sulfate and sulfuryl fluoride.

*Alkali metal fluosulfonates* may be prepared from the ammonium salt by evaporating a solution containing that salt and an alkali metal hydroxide or salt (13).

*Alkaline earth fluosulfonates* have not been prepared in pure condition. Aqueous reactions are unsatisfactory in this case because of hydrolysis. Other methods, such as treating barium fluoride with sulfur trioxide or fluosulfonic acid, have been unsuccessful. Crude barium fluosulfonate, or the equivalent mixture of barium fluoride and fluosulfonic acid, has been used as an intermediate in the preparation of sulfuryl fluoride.

*Heavy-metal fluosulfonates* have been prepared only in the form of complex coordination compounds such as the hexamminenickel, -zinc, -cadmium, and -cobalt fluosulfonates (15) and the ammonia, pyridine, and ethylenediamine complexes of copper (4). The fluosulfonates are isomorphous with the perchlorates, permanganates, and fluoborates.

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 (29) U.S. Pat. 2,430,963 (Nov. 18, 1947), R. Stevenson and W. E. Watson (to General Chemical Co.).  
 (30) U.S. Pat. 2,434,040 (Jan. 6, 1948), B. F. Hartman (to Socony-Vacuum Oil Co.).

W. S. W. McCARTER

**Tantalum Compounds.** See *Tantalum*.**Uranium Compounds.** See *Uranium*.**Zinc Fluoride.**

Zinc fluoride,  $\text{ZnF}_2$ , formula weight 103.38, is a hygroscopic white crystalline solid; m.p.  $872^\circ\text{C}$ .; sp.gr. 4.61; solubility in water, 1.516 grams/100 ml. saturated solution at  $25^\circ\text{C}$ . It is soluble in ammonia and hot acids. The tetrahydrate,  $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ , which is formed by treating the oxide or hydroxide with hydrofluoric acid, loses its water of crystallization at  $100^\circ\text{C}$ . Zinc fluoride is used in ceramic glazes, in galvanizing baths, as a wood preservative, and in making phosphors (see *Luminescent materials*).

F. D. LOOMIS

**FLUORINE COMPOUNDS, ORGANIC**

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Before the present century, publications in the field of fluorine chemistry were limited almost solely to those of Moissan. For the next three decades, the principal investigator was Swarts. However, the commercialization of certain chlorofluorohydrocarbons as refrigerating agents in household devices and air-conditioning equipment about 1930 furnished impetus for the increasing interest in the field. More recently, research in fluorination underwent a remarkable intensification, which may be attributed to the role of fluorine-containing compounds in the development of the atomic bomb during World War II. The extreme stability of highly fluorinated compounds to chemical action and heat is one of the principal incentives for the present wide scope of research on the preparation and properties of these substances. Of the enormous number of organic fluorine compounds known, only those are dealt with in this article that are of present commercial importance or give promise of usefulness. For a comprehensive table of organic fluorine compounds, see reference (10).

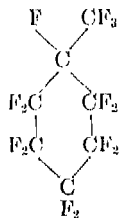
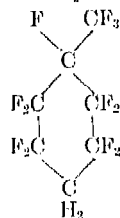
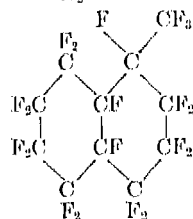
**Nomenclature**

Unfortunately, several systems of nomenclature for organic fluorine compounds have been used during the rapid expansion in this field. Perhaps the interest in

nomenclature and the attempts to develop wholly new systems for fluorocarbons (containing only fluorine and carbon) and other fluorine-containing compounds were a result of a realization of the potentially large number of compounds to be made and named. A simple and unified system for naming organic compounds having many fluorine atoms is obviously desirable.

Nine proposed systems of nomenclature were studied by an advisory committee of the Committee on Nomenclature of Organic Compounds of the American Chemical Society. A wide variety of compounds were named according to these systems by about fifty persons who had done research in the field of fluorine chemistry. As a result of these studies, the following conclusions and recommendations appear to be appropriate (systems (3) and (4) were recommended by the Subcommittee on Non-functional Derivatives). Examples of acceptable names are given in Table I.

TABLE I. Comparison of Acceptable Nomenclature Systems for Fluorine Compounds.

Compound	I.U.P.A.C.	C.A.	"Per"	"H"
$\text{CF}_3\text{CF}_2\text{CF}_3$	Octafluoropropane	Octafluoropropane	Perfluoropropane	—
$\text{CF}_3\text{CH}_2\text{CF}_3$	1,1,1,3,3,3-Hexafluoropropane	1,1,1,3,3,3-Hexafluoropropane	—	2H,2H-Hexafluoropropane
	(Trifluoromethyl)-undecafluorocyclohexane	(Trifluoromethyl)-undecafluorocyclohexane	Perfluoro-(methylecyclohexane)	—
	(Trifluoromethyl)-1,2,2,3,3,5,5,6,6-nonafluorocyclohexane	(Trifluoromethyl)-1,2,2,3,3,5,5,6,6-nonafluorocyclohexane	—	4H,4H-(Trifluoromethyl)-nonafluorocyclohexane
	Heptadecafluoro-decahydro-1-(trifluoromethyl)-naphthalene	Heptadecafluoro-decahydro-1-(trifluoromethyl)-naphthalene	Perfluoro-(1-methyl-decahydronaphthalene)	—
$\text{CF}_3\text{COOH}$	Trifluoroethanoic acid	Trifluoroacetic acid	Perfluoroacetic acid	—
$\text{CF}_3\text{CH}_2\text{COOH}$	3,3,3-Trifluoropropanoic acid	$\beta,\beta,\beta$ -Trifluoropropionic acid	—	2H,2H-Trifluoropropionic acid
$\text{CF}_3\text{CHO}$	Trifluoroethanal	Fluoral	Perfluoroacetaldehyde	—
$\text{CF}_3\text{CH}_2\text{OH}$	2,2,2-Trifluoroethanol	2,2,2-Trifluoroethanol	—	1H,1H-Trifluoroethanol

(1) The International Union of Pure and Applied Chemistry (I.U.P.A.C.) system of nomenclature is acceptable for the naming of fluorine-containing compounds.

(2) The *Chemical Abstracts* (C.A.) system of nomenclature (which differs only in certain respects from the I.U.P.A.C. system) is also acceptable for the naming of fluorine-containing compounds.

(3) The terms "perbromo," "perchloro," "perfluoro," and "periodo" may be applied to organic compounds or groups and shall denote substitution of all hydrogen atoms attached to carbon atoms except those whose substitution would affect the nature of the functional groups present. "Per" may refer to the whole word or to part of the word to which it is attached, but not to more than one word. Parentheses should be used where necessary to avoid ambiguity as to whether per refers to part of a word or to a whole word. There is a noticeable tendency to use the I.U.P.A.C. or C.A. names instead of "perfluoro" names for aliphatic compounds containing up to ten fluorine atoms.

It should be noted that this use of per excludes names in which per is preceded by other prefixes. Thus,  $\text{CF}_3\text{CClFCF}_3$  would be called 2-chloroheptafluoropropane and not 2-chloroperfluoropropane. The reason for this limitation is to avoid the implication that some other atom rather than hydrogen has been substituted.

(4) In halogenated compounds or groups, the position of the hydrogen atoms may be indicated by a prefix if the following conditions are met: (a) The hydrogen atoms are not part of a functional group. (b) Ordinarily the number of such hydrogen atoms will be not greater than four, and the ratio of such hydrogen atoms to the halogen atoms, which are of a single kind and not part of a functional group, will be not greater than one-third. This prefix shall consist of the numbers of the carbon atoms to which the hydrogen atoms are attached, each followed by the letter *H*.

(5) The use of the symbol  $\Phi$  to denote perfluoro is not acceptable because it resembles the symbol frequently used to represent the benzene ring, and because of the difficulty of typing. Examples of this system applied to some of the compounds given in Table I are:  $\Phi$ -propane; 2,2-dihydro- $\Phi$ -propane;  $\Phi$ -(methylcyclohexane);  $\Phi$ -acetic acid.

(6) The use of such terms as "for" and "fluor" as inserts in names now used is not acceptable. Examples of this system are: propforane (or propfluorane); 2,2-dihydropropforane; (methforyl)cyclohexforane; acetforic acid.

(7) The letter "f," like  $\Phi$ , could be used instead of perfluoro; however, it seems hardly worthwhile to introduce a new symbol just for completely fluorinated compounds. This seems especially true when the term per, as in perchloroethylene, is already in common usage. Also, the real problem lies in naming not only the completely fluorinated compounds, but those that contain a large number of fluorine atoms and only a few hydrogen atoms attached to carbon, as in  $\text{CF}_3\text{CHFCHF}(\text{CF}_2)_{10}\text{CF}_3$ . Therefore, it appears that the use of the symbol "f" to represent perfluorination will not be accepted. Examples of this system are: f-propane; 2,2-dihydro-f-propane; f-(methylcyclohexane); f-acetic acid.

Thus far, no satisfactory simple system has been conceived to delineate fluorine-containing compounds. Since the vast majority of these compounds—both those that are known and those that are likely to be made in the future—are organic substances, it would seem wise to follow the nomenclature rules applicable to organic compounds. A wholly new system of nomenclature for fluorine-containing substances does not appear to be compatible with good nomenclature. Certainly, by all accepted definitions, compounds such as  $\text{CF}_3\text{COOH}$ ,  $\text{CF}_3\text{CHO}$ , and even  $\text{CF}_3\text{CF}_3$  are derivatives of the organic compounds acetic acid, acetaldehyde, and ethane. It is hoped, therefore, that

chemists in general will follow the systems listed above as items (1) to (4) inclusive in naming fluorine-containing compounds of carbon.

### Physical Properties of Fluorinated Hydrocarbon Derivatives

The physical properties of fluorocarbons are "unusual," but no evidence has been brought forward to show that they are anomalous. That is to say, their properties appear to follow well-known laws and theories. The key to the behavior of these substances lies in the nature of the carbon-to-fluorine bond. Information concerning this bond may be obtained from the intensity with which various vibrational bands appear in the Raman and infrared spectra. The data indicate a very compact shell of valence electrons about the fluorine nucleus. These electrons, while sharing in the bond to the carbon atom, are very tightly bound to the fluorine nucleus; and this "unit" is extremely difficult to distort. This simple model is very useful in explaining the structural features and the chemical and physical properties of these molecules.

TABLE II. Atomic Refractions.

Atom	Atomic refraction	Atom	Atomic refraction
C.....	2.418	F.....	1.25
H.....	1.100	Cl.....	5.967
O (ether).....	1.643	Br.....	8.865
N (tertiary amine).....	2.840	I.....	13.900

Of course, a very tight electronic structure means a small value for the atomic polarizability of fluorine and hence a small atomic refraction. Just how small this quantity is may be seen from Table II, where it is compared with that for several other atoms of interest. It should be noted that, despite the larger number of electrons, the atomic polarizability (refraction) of fluorine is more nearly like that of hydrogen than the other halogens. As a direct consequence, the indexes of refraction of fluorocarbons are substantially lower than those of compounds of comparable molar volume. On the other hand, those compounds with comparable molar refractions, such as hydrocarbons, have substantially smaller molar volumes than the fluorocarbons, so that the same situation obtains. The net result is the fact that fluorocarbons have refractive indexes lower than those for any other known type of compound. Table III contains these data for a few compounds.

TABLE III. Physical Constants of Certain Fluorocarbons.

Formula	Name	B.p., °C.	$d_4^{20}$	$n_D^{20}$
C <sub>7</sub> F <sub>16</sub>	Perfluoro- <i>n</i> -heptane	82.4	1.7332	1.2618
C <sub>8</sub> F <sub>18</sub>	Perfluoro-(2,2,4-trimethylpentane)	104	1.8002 <sup>30</sup>	1.2733 <sup>30</sup>
C <sub>5</sub> F <sub>10</sub>	Perfluorocyclopentane	22	1.64 <sup>30</sup>	1.24 <sup>30</sup>
C <sub>7</sub> F <sub>14</sub>	Perfluoro(ethyleyclopentane)	75.1	1.7707	1.2772
C <sub>8</sub> F <sub>16</sub>	Perfluoro-( <i>o</i> -dimethylcyclohexane)	102.6	1.8672	1.2923
C <sub>6</sub> F <sub>6</sub>	Perfluorobenzene	81-82	1.612 <sup>25</sup>	1.3760

Intermolecular attraction is the result of dispersion forces plus the forces caused by permanent dipole moments. Except in molecules having relatively large dipole moments, the attractive forces are almost exclusively due to the dispersion effect,

which in turn depends upon the square of the molecular polarizability. Therefore, highly fluorinated molecules should have weak intermolecular forces or a low "internal pressure."

One consequence of this fact is low boiling points. The primary effect of the lower dispersion forces is seen in Table IV. The replacement of a chlorine atom by a

TABLE IV.

Chlorohydrocarbon	B.p., °C.	Chlorofluorohydrocarbon	B.p., °C.	Difference
$\text{CCl}_4$	77	$\text{CCl}_3\text{F}$	25	52
$\text{CHCl}_3$	61	$\text{CHCl}_2\text{F}$	9	52
$\text{CH}_2\text{Cl}_2$	40	$\text{CH}_2\text{ClF}$	-9	49
$\text{CH}_3\text{Cl}$	-24	$\text{CH}_3\text{F}$	-78	54

fluorine atom with its lower atomic polarizability (see Table II) results in a nearly constant drop of 50°C. in the boiling point. The same effect is seen in Table V where more than one atom of chlorine is replaced.

TABLE V.

Chloro-hydrocarbon	B.p., °C.	Fluoro-hydrocarbon	B.p., °C.	Difference per F atom
$\text{CH}_3\text{Cl}$	-24	$\text{CH}_3\text{F}$	-78	54
$\text{CH}_2\text{Cl}_2$	40	$\text{CH}_2\text{F}_2$	-52	46
$\text{CHCl}_3$	61	$\text{CHF}_3$	-83	48
$\text{CCl}_4$	77	$\text{CF}_4$	-128	51

Since the atomic polarizability of fluorine is comparable to that of hydrogen (Table II) it could be expected that fluorocarbons boil in the same temperature range as the corresponding hydrocarbons. This remarkable result is seen in the data of Table VI.

TABLE VI.

Hydrocarbon	B.p., °C.	Fluorocarbon	B.p., °C.
$\text{CH}_4$ .....	-161	$\text{CF}_4$ .....	-128
$\text{C}_2\text{H}_6$ .....	-88	$\text{C}_2\text{F}_6$ .....	-78
$\text{C}_3\text{H}_8$ .....	-45	$\text{C}_3\text{F}_8$ .....	-38
$\text{C}_4\text{H}_{10}$ .....	0.6	$\text{C}_4\text{F}_{10}$ .....	-5
$\text{C}_7\text{H}_{16}$ .....	98	$\text{C}_7\text{F}_{16}$ .....	82
$\text{C}_8\text{H}_{18}$ .....	80	$\text{C}_8\text{F}_{18}$ .....	82
$\text{C}_6\text{H}_{12}$ (cyclic).....	81	$\text{C}_6\text{F}_{12}$ (cyclic).....	52

Superimposed upon the dispersion effect is the effect caused by permanent dipole moments; this effect is nicely illustrated by the data for the fluorine compounds in Table V. On the other hand, the effect of the substantial incremental increase in the molecular polarizability (dispersion force) masks that of the rise and fall of the dipole moment on the boiling point of the corresponding chlorine compounds.

Other interesting physical properties of fluorocarbons owe their existence to the weak intermolecular forces. Thus, Trouton's constants and heats of vaporization are normal, and surface tensions, which are illustrated in Table VII, are low.

TABLE VII.

Compound	Surface tension at 20°C., dynes/cm.
Perfluoro- <i>n</i> -heptane.....	13.6
Perfluoro(methylcyclohexane).....	15.4
Perfluoro-( <i>p</i> -dimethylcyclohexane).....	16.3
<i>n</i> -Octane.....	21.8
Benzene.....	28.9
Methyl bromide.....	41.5
Water.....	72.8

Not many quantitative experimental data are available on the solubility of fluorocarbons. However, it is known that they are soluble in ether, other fluorocarbons, and chlorofluoro compounds; slightly soluble in aliphatic hydrocarbons; and insoluble or have limited solubility in water, alcohol, acetone, benzene, etc. As the molecular weight of the fluorocarbon increases, its solubility decreases, so that very high-molecular substances exhibit general insolubility. This behavior is also the consequence of the weak intermolecular forces in the fluorocarbons as compared to other substances of similar molar volume.

In contrast to the above phenomena, the viscosities of the fluorocarbons are considerably higher than those of the corresponding hydrocarbons. This is believed to be due to greater "stiffness" in the fluorocarbon chain, a consequence of the large repulsions between nonbonded fluorine atoms at close range, and the greater density of these substances. Fluorocarbons have a large viscosity index, that is, the viscosity drops rapidly with increasing temperature. The explanation for this behavior lies in the large decrease in density that occurs simultaneously. This results in a rapid increase in the "free space" or "holes" in the liquid and consequently a rapid increase in the fluidity. The viscosity of perfluoro-*n*-heptane at several temperatures is as follows:

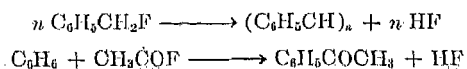
Temperature, °C.....	0.4	27.5	32.1	38.2	45.0
Viscosity, millipoises.....	13.67	8.61	8.05	7.33	6.64

### Reactions of Fluorinated Hydrocarbon Derivatives

On the basis of chemical behavior, organic fluorides may be divided into two main classes, those containing monofluorinated carbon groupings and those containing di- or trifluorinated carbon groupings. Monofluorides are unstable and tend to lose hydrogen fluoride, forming olefins, polymers, and other condensation products. On the other hand, saturated polyfluorides are very stable and exhibit little chemical activity. The stability of the polyfluorides is especially apparent when the halogens are grouped together. 1,1-Difluoroethane is stable, while 1,2-difluoroethane is unstable and tends to lose hydrogen fluoride.

**Monofluorides.** The reactions of the monofluorides are, in general, based on the ability of the molecule to lose an atom of fluorine or a molecule of hydrogen fluoride. Isomerization of a primary fluoride to form a secondary fluoride can be attained readily. Secondary and tertiary fluorides lose hydrogen fluoride more easily, but no isomerization is obtained.

Condensation reactions can occur in which the atom of fluorine comes from one molecule and the hydrogen atom from another (10):



In the latter case, a Friedel-Crafts type of condensation occurs without the use of the classical reagent, aluminum chloride.

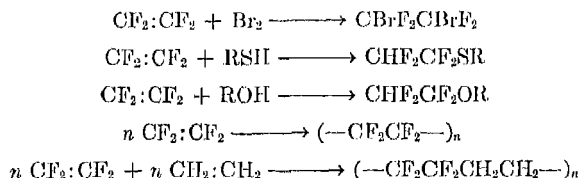
There are several cyclization reactions that use hydrogen fluoride as the condensing agent. The mechanism is assumed to be the formation of an intermediate acyl fluoride that reacts in a Friedel-Crafts fashion (10).

The polyfluorides have for convenience been further classified into saturated aliphatic, olefinic, aromatic, and fluorocarbons.

**Saturated Aliphatic Polyfluorides.** The inertness of this type of compound is especially apparent in the methane derivatives. For example, dichlorodifluoromethane can be treated with molten sodium with no evident signs of decomposition. This stability is extended to other halogen or hydrogen atoms on adjacent carbon atoms, which also resist hydrolysis or replacement. The chlorination of 1,1,1-trifluoropropane exemplifies the stabilizing effect of the  $-\text{CF}_3$  grouping, as the sequence of products is  $\text{CF}_3\text{CH}_2\text{CH}_2\text{Cl} \rightarrow \text{CF}_3\text{CH}_2\text{CHCl}_2 \rightarrow \text{CF}_3\text{CH}_2\text{CCl}_3 \rightarrow \text{CF}_3\text{CHClCCl}_3 \rightarrow \text{CF}_3\text{CCl}_2\text{CCl}_3$ . It is possible to obtain reactions with halogen atoms that are two or more carbon atoms removed from the carbon atom completely substituted by fluorine; for example, 3-bromo-1,1,1-trifluoropropane reacts with magnesium to form a Grignard reagent.

Under extreme conditions the pyrolysis of aliphatic fluorides gives condensation products. At 400–700°C., chlorodifluoromethane forms tetrafluoroethylene as the principal product, perfluorocyclobutane ( $\text{C}_4\text{F}_8$ ), perfluorocyclopentane ( $\text{C}_5\text{F}_{10}$ ), and a series of compounds of formula  $\text{H}(\text{CF}_2)_n\text{Cl}$ .

**Olefinic Polyfluorides.** This type of compound undergoes chemical reaction more readily than saturated polyfluorides. Addition to the unsaturated linkages can be effected, and much work in this field is in progress. The following equations will serve to illustrate some of the addition reactions possible with tetrafluoroethylene as an example:



Much research is being done in the field of fluorine-containing polymers, as these compounds exhibit unusual resistance to heat and chemical attack.

**Aromatic Polyfluorides.** The reactions of the (perfluoroalkyl)benzenes such as benzonitrifluoride,  $\text{C}_6\text{H}_5\text{CF}_2$  (see p. 757), are typical of an aromatic compound containing a strong meta-directing group. The ease of substitution in the ring decreases with an increase in the number of completely fluorinated alkyl groups.

**Chlorination.** Reaction of benzonitrifluoride with chlorine to produce all the possible ring-substituted derivatives is best conducted in the liquid phase at 100°C. with ferric chloride as a catalyst. The reaction temperature is higher than that generally used for the chlorination of toluene. Benzonitrifluoride has been chlorinated in the presence of light to produce 1,2,3,4,5,6-hexachloro-1-(trifluoromethyl)cyclohexane. The reaction is slow, requiring several days for its completion.

Bis(trifluoromethyl)benzenes ( $\alpha, \alpha, \alpha, \alpha', \alpha', \alpha'$ -hexafluoroxylens (*C.A.*)) can be chlorinated in the vapor phase at temperatures ranging from 250 to 350°C. In this reaction, a mixture of chlorine and the organic compound is passed over a catalyst composed of activated carbon impregnated with ferric chloride. By use of a stripping column and careful control of the amount of chlorine, it is possible to obtain predominantly any one of the four possible substitution isomers (15).

**Bromination.** A satisfactory bromination procedure comprises reaction of the trifluoromethyl-substituted benzenes with a mixture of bromine, chlorine, and antimony pentachloride at 50–200°C. (21). In the case of benzonitrifluoride, the reaction is conducted at 25–50°C. and comprises mixing the organic compound with antimony pentachloride and simultaneously adding bromine and chlorine to the reaction mixture. The presence of chlorine converts the hydrogen bromide formed to bromine and hydrogen chloride and maintains the pentavalent state of the antimony chloride. The bromine enters in the meta position. Bromination of bis(trifluoromethyl)benzenes is more difficult and is conducted at autogenous pressures at temperatures ranging from 100 to 200°C.

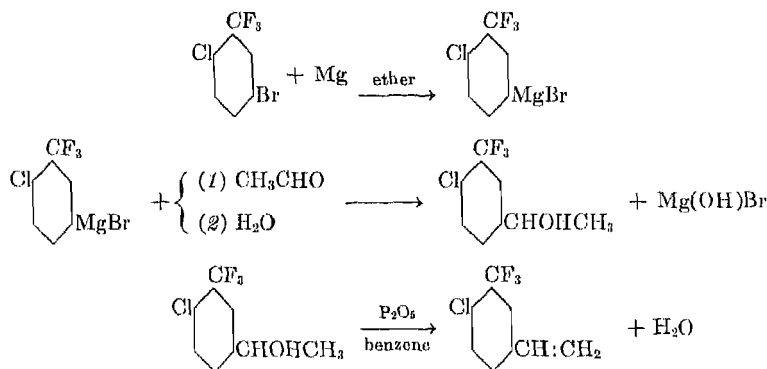
**Preparation of Ether Derivatives.** (Trifluoromethyl)aryloxyalkanes are prepared by reaction of a sodium alkoxide with a chloro- or bromo-substituted (trifluoromethyl)benzene. The organic compound and the sodium alkoxide are placed in a solvent of the alcohol corresponding to the alkoxide and the mixture is heated until reaction occurs. In most cases in which the halogen is ortho or para to the trifluoromethyl group, the reflux temperature of the mixture is sufficient to ensure reaction. In the

case of a meta halogen, the temperature must be higher, and pressure vessels are necessary. If the reaction is conducted under anhydrous conditions, little hydrolysis of the trifluoromethyl group occurs. However, the presence of water causes rapid hydrolysis due to the relatively high temperature and strong base employed.

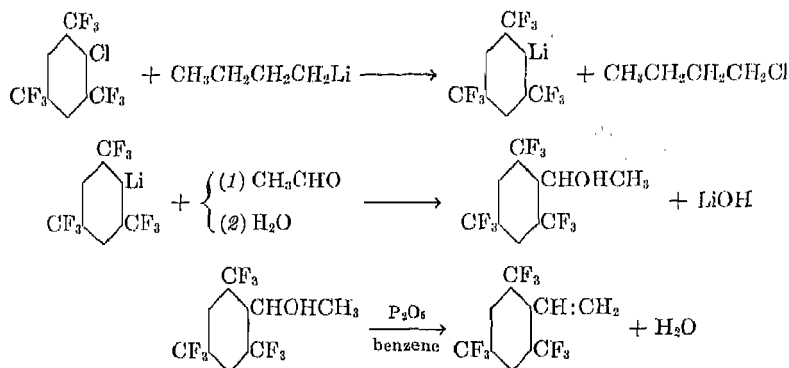
*Preparation of Grignard Reagents.* Bromo derivatives of (trifluoromethyl)benzenes can be converted to Grignard reagents in the classical manner with ease (see *Grignard reaction*). The Grignard reagents thus formed have been used to prepare derivatives of (trifluoromethyl)benzenes, including alcohols, acids, styrenes, phenols, and biphenyls. Bromochloro(trifluoromethyl)benzenes containing bromine and chlorine atoms on adjacent carbon atoms failed to form Grignard reagents, while those with the halogens separated reacted easily. Compounds such as 5-bromo-2,4-dichlorobenzotrifluoride and 3-bromo-4-chlorobenzotrifluoride failed to form Grignard reagents, but 5-bromo-2,3-dichlorobenzotrifluoride and 5-bromo-2-chlorobenzotrifluoride reacted readily.

It was not possible to form a Grignard reagent from a halo-1,3,5-tris(trifluoromethyl)benzene (halo- $\alpha, \alpha, \alpha', \alpha', \alpha', \alpha'', \alpha''$ -nonafluoromesitylene (C.A.)). However, the lithium derivative, which could be used in further syntheses, was produced.

*Styrenes.* Various trifluoromethyl-substituted styrenes were prepared from benzotrifluoride, bis(trifluoromethyl)benzenes, and 1,3,5-tris(trifluoromethyl)benzene and polymerized by an emulsion technique. In general, the method of preparation is illustrated by the following equations:



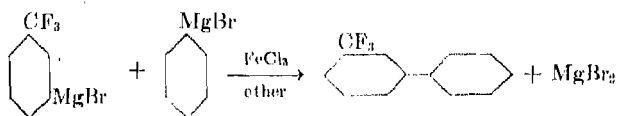
In the case of 1,3,5-tris(trifluoromethyl)benzene, the styrene was prepared by means of the lithium derivative as follows:



The  $\alpha$ -methyl-substituted styrenes derived from mono- and bis(trifluoromethyl)benzenes were prepared by reaction of acetone with the Grignard reagent. However, the lithium derivative of 1,3,5-tris(trifluoromethyl)benzene failed to react.

*Biphenyls* (diphenyls). The trifluoromethyl-substituted biphenyls were prepared by the intermolecular condensation of the appropriate (trifluoromethyl)phenylmagnesium bromides or by the condensation of a (trifluoromethyl)phenylmagnesium bromide with phenylmagnesium bromide in the presence of ferric chloride:





Since phenylmagnesium bromide condenses more readily with itself than with (trifluoromethyl)-phenylmagnesium bromides, higher temperatures and a larger quantity of ferric chloride were employed in the preparation of the unsymmetrical (trifluoromethyl)biphenyls. The use of extensive quantities of the condensing agent produced abnormally large quantities of tarlike polymers.

**Nitration.** Nitration of both benzotrifluoride and bis(trifluoromethyl)benzenes produces the mononitro derivatives. In the case of benzotrifluoride, dinitration is possible but requires such vigorous conditions that low yields are obtained. The nitration of the bis(trifluoromethyl)benzenes is extremely difficult although reasonable yields can be obtained by the use of a liquid-phase technique.

The nitro compounds have been reduced to the amines, and both *m*-nitrobenzotrifluoride and *m*-(trifluoromethyl)aniline ( $\alpha,\alpha,\alpha$ -trifluoro-*m*-toluidine (C.A.)) are available commercially. Diazotization of the latter compound followed by hydrolysis produces *m*-(trifluoromethyl)phenol ( $\alpha,\alpha,\alpha$ -trifluoro-*m*-cresol (C.A.)). This method was found to be superior to that comprising oxygenation of the corresponding Grignard reagent.

**Fluorocarbons.** Since the fluorocarbons in general resist attack by chemical agents, little is known of their chemical properties beyond the fact that they do not enter into chemical action with other substances under ordinary conditions. Fragmentary evidence is available which indicates that some of the fluorine atoms in a fluorocarbon are not as firmly held as others. Hydrolysis studies using aqueous base showed that slight hydrolysis of a fluorocarbon does occur, but no identifiable organic products could be isolated. The reaction of fluorocarbons with hydrogen at elevated temperatures produces lower-molecular, hydrogen-containing fluoroalkanes. At high temperatures, the action of bromine on saturated fluorocarbons such as octafluoropropane produced carbon-to-carbon fission with the formation of lower-molecular-weight bromofluoroalkanes. Fluorocarbons react with sodium or potassium at 300–400°C. and decompose in the presence of sodium dissolved in liquid ammonia.

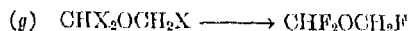
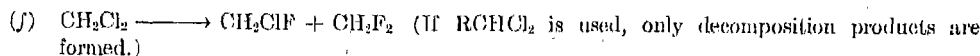
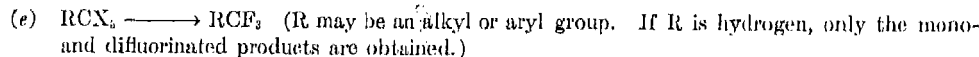
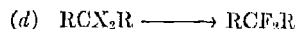
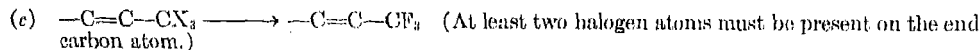
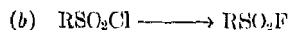
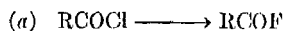
Unsaturated fluorocarbons generally exhibit much more chemical activity than the saturated compounds. For example, tetrafluoroethylene is very reactive when compared to hexafluoroethane. In fact, tetrafluoroethylene exhibits an order of reactivity superior to that of the other perhalogenated olefins such as tetrachloroethylene.

## Methods of Fluorination

### HALOGEN EXCHANGE

The exchange of another halogen atom in an organic compound for a fluorine atom of the fluorinating agent is the most widely used method of fluorination. The relative ease of replacement follows the general order  $\text{I} > \text{Br} > \text{Cl}$ . Various metallic fluorides and hydrogen fluoride are used as fluorinating agents.

*Antimony trifluoride*,  $\text{SbF}_3$  (see p. 676), does not in general act efficiently when used alone. However, it can be used in the following reactions (10):



The limitations of the reagent are many. It cannot be used successfully to replace a single halogen atom with the exceptions shown in reactions (a), (b), and (f) or halogen attached to a double-bonded carbon atom. Fluorination of halogenated esters, sulfides, ketones, acids, and aldehydes produces decomposition products derived from rupture of the carbon chains.

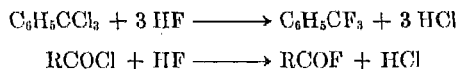
The effectiveness of antimony trifluoride can be increased by adding chlorine or antimony pentachloride to the reaction mixture in quantities equivalent to about 10% by weight of the antimony trifluoride. The formation of either  $\text{SbCl}_2\text{F}_3$  or  $\text{SbF}_5 \cdot \text{SbCl}_5$ , both of which are effective fluorinating agents, probably accounts for the increased activity of the reagent. The reagent is used for the replacement reactions listed above. A more rapid reaction occurs and better yields are obtained than with antimony trifluoride alone. In general, the same limitations apply as given previously (10).

*Antimony pentafluoride*,  $\text{SbF}_5$  (see p. 677), is a very active reagent and is generally used to fluorinate only completely halogenated compounds, since those containing hydrogen as well as halogen undergo extensive decomposition. When a completely halogenated olefin or aromatic compound is used, addition as well as replacement is obtained (22). Thus, hexachlorobenzene gives a cyclohexene derivative:



The preparation of completely fluorinated aromatics may be illustrated by hexafluorobenzene, which can be prepared by reaction of hexachlorobenzene with bromine trifluoride and antimony pentafluoride, followed by dehalogenation with zinc dust to produce the desired product, together with perhalo derivatives of cyclohexadiene and cyclohexene (18).

*Hydrogen fluoride*, HF (see p. 695), is a comparatively weak fluorinating agent and can be used to replace active halogens (16,24):

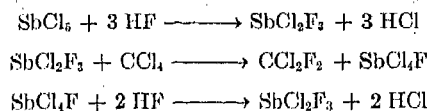


However, under vigorous reaction conditions, it is possible to replace vinyl-type halogens (11):



This reaction probably proceeds first through addition of hydrogen fluoride to the double bond, followed by replacement of the two chlorine atoms.

Hydrogen fluoride is also used together with antimony pentachloride to form a fluorinating agent comparable in activity with the reagent produced by adding antimony pentachloride to antimony trifluoride (19). In this manner, it is possible to obtain a continuous fluorination process whose probable course is illustrated by the following equations:

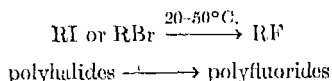


Since the antimony halides are re-used, the fluorinating agent in effect is hydrogen fluoride.

*Mercuric fluoride*,  $\text{HgF}_2$ , may be prepared by the reaction of mercuric chloride with fluorine, or it may be prepared *in situ* by adding red mercuric oxide to a mixture of

hydrogen fluoride and the material to be fluorinated. The reagent is generally prepared in this manner since this procedure is more easily conducted in the laboratory.

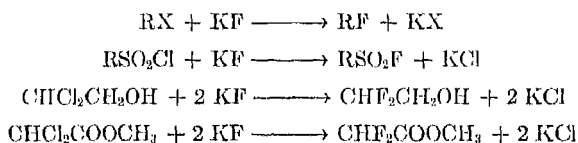
Mercuric fluoride is effective in the following conversions (4,10):



The alkyl chlorides and polychlorides react very slowly, permitting compounds such as chloroform or methylene chloride to be used as solvents. Oxygen-containing compounds like esters, ethers, and alcohols prevent the reaction from occurring.

*Mercurous fluoride*,  $\text{HgF}_2$ , which is prepared by the reaction of freshly prepared mercurous carbonate with hydrofluoric acid, is a weaker agent than mercuric fluoride and has been used to convert alkyl iodides to alkyl fluorides; alkyl bromides and chlorides are less affected. The polyhalides undergo dehalogenation to form olefins and mercury salts. The addition of chlorine or iodine to the mercurous fluoride increases the activity of the reagent, owing to the formation of the complex  $\text{HgF}_2 \cdot \text{HgX}_2$  (4,10).

*Potassium fluoride*,  $\text{KF}$  (see p. 721), can be used to convert alkyl halides and sulfonyl chlorides to the corresponding fluorides, and to fluorinate halogenated alcohols, acids, and esters (6,9):



The rodenticide sodium fluoroacetate is prepared by reaction of potassium fluoride with an ester of chloroacetic acid followed by hydrolysis with caustic (see p. 764).

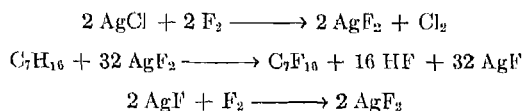
#### SUBSTITUTION OF HYDROGEN

The use of *fluorine* as a fluorinating agent in a manner similar to the use of the other halogens is difficult since the reactions are very vigorous. The substitution of fluorine for hydrogen in a hydrocarbon is a highly exothermic reaction owing to the high heat of formation of hydrogen-to-fluorine and carbon-to-fluorine bonds. The heat of reaction is greater than the energy required to break a carbon-to-carbon linkage, and the yields of compounds having the same carbon skeletal arrangement as the starting material are generally low. The reaction of carbon with fluorine gives mostly carbon tetrafluoride, as well as other materials identified as  $\text{C}_3\text{F}_8$ ,  $\text{C}_4\text{F}_{10}$ ,  $\text{C}_6\text{F}_{12}$ , and  $\text{C}_7\text{F}_{14}$ . Hydrocarbons can be fluorinated in the vapor phase in a metal apparatus in which fluorine diluted with nitrogen is dispersed through a copper gauze that serves as a medium for the dissipation of heat. A variety of reaction products obtained by the replacement of hydrogen and the fission of the carbon-to-carbon bonds are obtained (2,5). Benzene, on reaction with fluorine, gives many products, among which are  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $\text{C}_4\text{F}_{10}$ , and the cyclic  $\text{C}_5\text{F}_{10}$ ,  $\text{C}_6\text{F}_{12}$ ,  $\text{C}_6\text{HF}_{11}$ , and  $\text{C}_{12}\text{F}_{22}$  (2,5).

It has been proposed that fluorine reacts with organic compounds by a chain mechanism involving fluorine atoms (3). For example, when 4-chloro-1,3-bis(trifluoromethyl)benzene,  $\text{C}_6\text{H}_3\text{Cl}(\text{CF}_3)_2$ , was treated with fluorine, it yielded both addition products ( $\text{C}_6\text{H}_3\text{ClF}_2(\text{CF}_3)_2$  and  $\text{C}_6\text{H}_3\text{ClF}_4(\text{CF}_3)_2$ ) and addition and substitution products ( $\text{C}_6\text{H}_3\text{F}_7(\text{CF}_3)_2$ ,  $\text{C}_6\text{F}_{10}(\text{CF}_3)_2$ ,  $\text{C}_6\text{F}_{11}\text{CF}_3$ , and  $\text{C}_6\text{F}_{12}$ ).

*Metal fluorides* generally used for the replacement of hydrogen are silver difluoride, cobalt trifluoride, manganese trifluoride, lead tetrafluoride, cerium tetrafluoride (prepared by fluorination of the trifluoride), bismuth pentafluoride, and thallium trifluoride. Of these, silver difluoride is the most active and is a useful agent for laboratory preparation of fluorocarbons (8). Cobalt trifluoride is used commercially (see pp. 693, 753).

*Silver difluoride* may be conveniently prepared by passing fluorine over silver chloride and may be similarly regenerated from the silver monofluoride formed during the fluorination of the hydrocarbon (17):

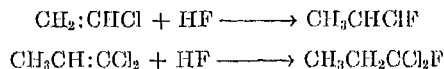


The silver difluoride therefore serves as a fluorine carrier. The procedure is more advantageous than direct fluorination in that control of the reaction is easier and the yield of fluorocarbon in which the carbon skeletal arrangement of the starting material is retained is much higher. Two general techniques have been employed, liquid-phase and vapor-phase fluorinations. The choice of technique depends upon the nature of the starting material (1).

#### ADDITION TO MULTIPLE BONDS

The addition of hydrogen fluoride to unsaturated linkages has received considerable attention as a method of producing organic fluorides. The process possesses the advantages of both the low cost of the hydrogen fluoride when compared to other fluorinating agents and the reduced cost of the organic reagent as compared to the usual intermediate halides. The reactions can be conducted at atmospheric pressure, usually in the vapor phase, or at superatmospheric pressures, in autoclaves where either vapor or vapor-liquid phases may be obtained. When anhydrous conditions are used, steel equipment is generally satisfactory; however, at elevated temperatures, nickel has proved to be more satisfactory.

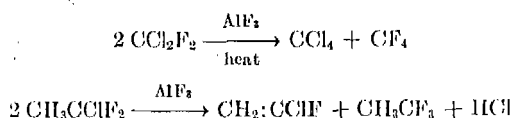
The reaction with olefins usually gives a secondary or tertiary fluoride, but difficulty is encountered in the preparation of tertiary fluorides, which are easily decomposed by heat or hydrolytic agents. When the olefin is halogenated on one of the double-bonded carbon atoms, addition is more complete; for example, vinyl chloride yields 1-chloro-1-fluoroethane, and 1,1-dichloropropene forms 1,1-dichloro-1-fluoropropane, in excellent yields:



In general, Markovnikov's rule of addition is strictly followed and reversal of the addition is very difficult (10). The reactions may be catalyzed by such compounds as boron trifluoride, manganese dioxide, cobaltic oxide, mercury salts, chromium trifluoride, oxygen, and salts of zinc and nickel.

#### DISPROPORTIONATION

Methods of producing fluorohydrocarbons by disproportionation of chlorofluorohydrocarbons have been patented (25):



## ELECTROCHEMICAL

A new method of fluorination comprises the electrolysis of a solution of the organic material in hydrogen fluoride. The solution is conducting in most cases because of the ionization of the organic material, but compounds such as hydrocarbons require the addition of a third substance to impart conductivity. The products are isolated from the cell gases or are drained from the bottom of the cell, depending upon their boiling points (23).

The cells can be constructed of any ordinary structural material, such as steel or copper, not readily attacked by hydrogen fluoride. The anodes are constructed of nickel, and the cell body itself serves as a cathode. The voltages used are in the range between 5 and 8, though voltages between 5 and 6 are preferred. The current density is about 0.02 amp. per square centimeter.

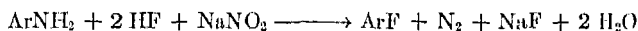
Generally, the cells operate without the generation of elementary fluorine. As higher potentials are used, fluorine is produced, and extensive corrosion of the electrodes occurs.

The process has been extended to include preparation of fluorocarbons, perfluorinated ethers, perfluorinated acids, and derivatives of amines in which all hydrogen has been replaced by fluorine.

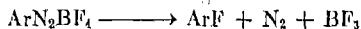
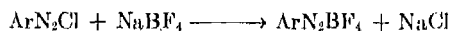
## DIAZOTIZATION

Aromatic fluorides are generally prepared by diazotization of an amine, followed by decomposition of the diazonium salt to form the fluoride. Two modern methods are described by which good yields of the aromatic fluorides can be obtained (4).

The first method comprises mixing the amine and hydrogen fluoride and then adding sodium nitrite. Heating the reaction mixture produces the desired fluoro aromatic:



The second method consists of preparing the diazonium fluoborate from the amine, followed by controlled decomposition of the salt with heat to produce the aromatic fluoride:



For the preparation of completely fluorinated aromatics, see p. 747.

## REPLACEMENT OF HYDROXYL GROUPS

The reaction of an alcohol with hydrogen fluoride to produce an alkyl fluoride is not a widely used method of fluorination (10):



The reaction proceeds more slowly than corresponding halogen-exchange reactions, and the product is quite often unstable, making preparation and purification difficult.

The reaction can be accelerated by the use of beryllium fluoride when excess hydrogen fluoride or sodium acid fluoride is used as the fluorinating agent.

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### PHYSICAL PROPERTIES OF FLUORINATED HYDROCARBON DERIVATIVES

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E. T. MCBEE AND O. R. PIERCE

W. F. EDGEELL (Physical Properties of Fluorinated Hydrocarbon Derivatives)

### Fluorinated Hydrocarbons.

Fluorinated hydrocarbons of technical interest are those in which all, or almost all, of the hydrogen has been replaced by fluorine alone or by fluorine and other halogens.

#### Aliphatic Fluorocarbons.

*Properties.* The physical properties of the fluorocarbons are illustrated in Table I. Compounds containing only fluorine and carbon, when pure, are characterized by extreme chemical inertness at ordinary temperatures. They react with molten alkali metals; strong acids or oxidizing agents have no effect on them, and alkaline reagents react only slowly even at elevated temperatures. The more complex fluorocarbons start to decompose somewhat at about 400°C. and can be made to react partially with various metals and hydrogen at temperatures above 500°C.

TABLE I. Physical Properties of Fluorocarbons.

Formula	Chemical name	Formula wt.	M.p., °C.	B.p., °C.	$d_4^{20}$	$n_D^{20}$	Ref.
CF <sub>4</sub>	Tetrafluoromethane (carbon tetrafluoride)	88.01	-184	-128	1.62 <sup>-130</sup>	—	(9)
C <sub>2</sub> F <sub>6</sub>	Hexafluoroethane	138.02	-101	-78	1.607 <sup>-78</sup>	—	(9)
C <sub>3</sub> F <sub>8</sub>	Octafluoropropane	188.03	-183	-38	1.45 <sup>0.2</sup>	—	(6,12)
C <sub>4</sub> F <sub>10</sub>	Decafluoro- <i>n</i> -butane	238.04	< -80	-1.7	1.47	—	(4,8)
C <sub>5</sub> F <sub>12</sub>	Perfluoro- <i>n</i> -pentane	288.05	-126	29	1.6233	1.245	(13)
C <sub>6</sub> F <sub>14</sub>	Perfluoro- <i>n</i> -hexane	338.06	< -74	58	1.68	—	(15)
C <sub>7</sub> F <sub>16</sub>	Perfluoro- <i>n</i> -heptane	388.07	-57	82.4	1.7332	1.2618	(4)
C <sub>6</sub> F <sub>12</sub>	Perfluorocyclohexane	300.06	50	50-52	1.684 <sup>30</sup>	1.2685 <sup>30</sup>	(5)
C <sub>8</sub> F <sub>18</sub>	Perfluoro(dimethylcyclohexane)	400.08	< -40	102	1.853	1.2858 <sup>30</sup>	(2,5)
C <sub>14</sub> F <sub>34</sub>	Perfluorotetradeca- <i>h</i> ydro-phenanthrene	624.14	< -40	205	2.0197	1.3315	(5)

The fluorination of hydrocarbon mixtures such as those occurring in petroleum lubricating oil fractions gives a mixture of products similar in physical properties to lubricants. The physical properties of such mixtures are shown in Table II (2).

TABLE II. Typical Properties of Fluorocarbon Liquids.

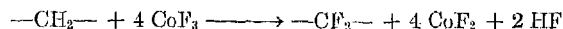
Empirical formula, av. ....	C <sub>12</sub> F <sub>26</sub>	C <sub>14</sub> F <sub>30</sub>	C <sub>21</sub> F <sub>44</sub>
Boiling range at 10 mm. Hg, °C. ....	20-65	65-130	130-240
$n_D^{20}$ .....	1.3082	1.3171	1.3430
$d_4^{25}$ .....	1.922	1.994	2.0
Viscosity, centipoises			
At 38°C. ....	1.80	7.69	2610
At 99°C. ....	0.63	1.42	14.1
Pour point, °C. ....	-30	-30	20
Dielectric constant. ....	—	2.02	—

The fluorocarbons have extremely low internal pressures (7,10) and therefore tend to be insoluble in both polar and nonpolar liquids. The fluorocarbons boiling above 130°C. at 10 mm. are insoluble in such solvents as carbon tetrachloride, methanol, acetone, benzene, and ethyl acetate. The lower-boiling fluorocarbons tend to be

soluble in chlorinated hydrocarbons, particularly in chlorofluorohydrocarbons such as 1,1,2-trichloro-1,2,2-trifluoroethane,  $\text{CCl}_2\text{FCClF}_2$ .

Most fluorocarbons, when pure, are nontoxic, as would be expected from their chemical inertness and low solubility. However, some toxic fluorocarbons are known, and many of the by-products obtained in their manufacture and many of their thermal decomposition products are extremely toxic. They should, therefore, be handled with caution, particularly to avoid inhalation.

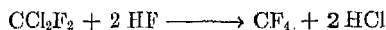
*Manufacture.* Fluorocarbons can be produced on a large scale by direct fluorination by means of a high-valence metal fluoride; for example (3):



This method has been used to prepare fluorocarbons containing from one to more than twenty carbon atoms, starting with the corresponding hydrocarbons. High yields are obtained from the hydrocarbons up to  $\text{C}_{10}$ , but the higher-boiling hydrocarbons usually suffer some carbon-to-carbon fission during the reaction with loss in yield. The reaction is usually carried out in horizontal, mechanically agitated, steel reactors containing a bed of powdered cobalt trifluoride (1), and it proceeds smoothly at temperatures between 150 and 350°C., depending upon the boiling point of the hydrocarbon. The cobalt difluoride formed is reconverted to cobalt trifluoride by elementary fluorine at similar temperatures and in the same reactor.

Fluorocarbons have also been made by the electrolysis of solutions of alcohols, acids, and amines in anhydrous hydrogen fluoride. For example, electrolysis of a solution of acetic acid in anhydrous hydrogen fluoride using a nickel anode gives fluorocarbon (trifluoromethane),  $\text{CHF}_3$ , and carbon tetrafluoride,  $\text{CF}_4$ , as well as carbon dioxide and oxygen fluorides (11). Other fluorocarbons can be similarly prepared from the appropriate acids or alcohols.

The simpler fluorocarbons can be made by reaction of anhydrous hydrogen fluoride with a chlorofluorocarbon at elevated temperatures; for example (14):



*Uses.* The lower members of the fluorocarbon series have been suggested for use as refrigerants. Their low toxicity, chemical inertness, and nonflammability are characteristics desirable in such use (see *Refrigeration*).

The high-boiling fluorocarbons, particularly those obtained by fluorination of mixed hydrocarbons, have viscosity and density characteristics similar to lubricants. They are used for lubrication purposes, particularly where it is necessary that they be in contact with strong chemical reagents and solvents. Their chemical inertness permits their use even in direct contact with strong acids such as sulfuric and nitric acids, corrosive oxidizing agents (including chlorine), and corrosive solvents (even sulfur chlorides). Their low solubility permits their use as lubricants where organic solvents are handled, even when reactive chemicals are also present.

Tetrafluoroethylene,  $\text{CF}_2\text{:CF}_2$ , which is produced by pyrolysis of chlorodifluoromethane (Freon-22) at 250°C., polymerizes under pressure to yield a solid inert plastic called Teflon (see *Resins and plastics containing halogen*).

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### Aliphatic Chlorofluorocarbons and Other Chlorofluorohydrocarbons.

Hydrocarbons containing fluorine and another halogen often have chemical and physical properties approaching those of the fluorocarbons. The possibility of varying the fluorine, chlorine, and hydrogen contents of the simple substituted hydrocarbons permits a wide variation in physical properties. In this way a series of useful commercial products have been developed.

*Properties.* The physical properties of the commercially important low-boiling chlorofluorohydrocarbons are shown in Table I. The chlorofluorohydrocarbons of

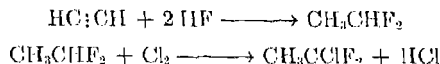
TABLE I. Physical Properties of Chlorofluoro- and Fluorohydrocarbons.

Formula	Trade name	M.p., °C.	B.p., °C.	$d_4^{20}$	Toxicity <sup>a</sup>	Ref.
CF <sub>4</sub>	Freon-14	-184	-128	1.62-1.63	Group 6	(5)
CClF <sub>3</sub>	Freon-13	-182	-82	1.703-1.70	Group 6	(5)
CHClF <sub>2</sub>	Freon-22	-160	-40.80	1.2130	Group 5-A	(9)
CCl <sub>2</sub> F <sub>2</sub>	Freon-12	-158	-29.8	1.326	Group 6	(7)
CH <sub>3</sub> CHF <sub>2</sub>	Genetron-100	-117	-24.7	0.912 <sup>19</sup>	—	—
CH <sub>3</sub> CClF <sub>2</sub>	Genetron-101	-131	-9.0	1.12 <sup>25</sup>	—	—
CClF <sub>2</sub> CClF <sub>2</sub>	Freon-114	-94	3.55	1.470	Group 6	(7)
CCl <sub>3</sub> F	Freon-11	-111	23.77	1.487	Group 5	(7)
CCl <sub>2</sub> FCClF <sub>2</sub>	Freon-113	-35	47.57	1.576	Group 4-A	(7,8)
CF <sub>3</sub> CCl:CCl <sub>2</sub>	—	-114.7	88.3	1.6188	—	(2)
CF <sub>3</sub> CCl:CClCF <sub>3</sub>	—	-67.3	67.8	1.6233	—	(3)

<sup>a</sup> Underwriters' Laboratories classification Group 6 indicates the lowest toxicity, and lower numbers indicate higher toxicity.

technical importance are relatively inert chemically, particularly in the absence of moisture. They do not react with most metals below temperatures of 200°C. or with acids or oxidizing agents. They react very slowly with alkalis in the presence of water and can be decomposed with molten alkali metals, particularly when dissolved in liquid ammonia. They are partially decomposed at temperatures above a red heat. In chemical properties, therefore, they are quite similar to the fluorocarbons, although somewhat less stable at elevated temperatures.

*Manufacture.* Chlorofluorohydrocarbons are produced technically by one of two reactions. In one, acetylene and hydrogen fluoride react to form 1,1-difluoroethane (12,14), which is then treated with chlorine to give a number of products such as 1-chloro-1,1-difluoroethane (16,17):



The second important technical method is based on the reaction of a chlorohydrocarbon with anhydrous hydrogen fluoride in the presence of an antimony halide catalyst (10):



The starting material and the degree to which chlorine is substituted by fluorine can be varied to give a variety of products. The fluorination is accomplished by passing a mixture of the chlorohydrocarbon, for example, carbon tetrachloride, and hydrogen fluoride into a steel vessel containing a mixture of antimony chlorides and fluorides. The reaction proceeds smoothly; the evolved lower-boiling fluorinated product and hydrogen chloride are separated from each other and from the starting materials by fractional distillation (13). The substitution of fluorine for chlorine proceeds stepwise, and the degree of fluorination is controlled by the temperature and pressure of the reactants and by the ratio of hydrogen fluoride to chlorohydrocarbon fed to the catalyst. The reactivity of chlorohydrocarbons varies considerably, and conditions must be adjusted to accomplish the desired degree of fluorination (15).

*Uses.* Most of the chlorofluorohydrocarbons of commercial interest are low-boiling liquids. Their principal use has been as refrigerants (see *Refrigeration*).

Low-boiling chlorofluorohydrocarbons are also used extensively as propellants for production of aerosols (1,11). The active ingredient, for example, an insecticide, is dissolved in the propellant and is stored in a low-pressure container. The pressure of the propellant forces the solution into the atmosphere as a spray, and the evaporation of the fine droplets produces a stable aerosol suspension. In this form, more effective use of an insecticide is obtained. The chlorofluorohydrocarbons are similarly used as propellants for spraying diverse materials such as floor wax, paint, cosmetic preparations, and perfumes. The requirements of nonflammability, negligible toxicity, and freedom from objectionable odor required in an aerosol propellant have been found only among these chlorofluorohydrocarbons.

Liquid and solid chlorofluorohydrocarbons have also been made by polymerization of chlorofluoroethylenes, particularly chlorotrifluoroethylene (trifluorovinyl chloride,  $\text{CF}_2\text{:CClF}$ , obtained by dechlorination of 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) with zinc. A plastic solid (Kel-F, Fluorothene), which has good mechanical properties and high resistance to chemical reagents, has been obtained in this manner (see *Resins and plastics containing halogens*). Liquid polymeric products are obtained from the polymerization of chlorotrifluoroethylene in the presence of a solvent or telomerizing agent such as chloroform (4,6). A mixture of liquid products with a wide spread in physical properties from thin liquids to greasy solids can be obtained; products of this type have been produced and sold under the name Fluorolubes. They have the characteristic chemical inertness of the simpler chlorofluorohydrocarbons and have a high measure of resistance to solvents, though they are more soluble, generally, than the fluorocarbons. Their principal use has been in applications where inertness

to chemical reagents or oxidizing conditions is necessary, for example, as lubricants and sealants for use on equipment handling oxygen, concentrated hydrogen peroxide, and nitric acid.

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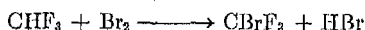
### Aliphatic Bromofluorocarbons and Iodofluorocarbons.

**Bromofluorocarbons.** A number of compounds containing only the elements carbon, fluorine, and bromine have been prepared, the most interesting being the monobromofluorocarbons. Like the corresponding chlorofluorocarbons or fluorocarbons, they are inert chemically but are not as stable. The compounds exhibit less stability as the ratio of bromine to fluorine increases. The physical properties of some of the lower members of the series are given in Table I.

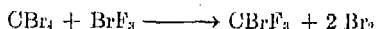
TABLE I. Physical Properties of Bromofluorocarbons.

Formula	Chemical name	Formula wt.	M.p., °C.	B.p., °C.	$d_4^{25}$	Ref.
$\text{CBrF}_3$	Bromotrifluoromethane	148.93	-180	-59	1.58	(1,2)
$\text{CBr}_2\text{F}_2$	Dibromodifluoromethane	209.84	-80	24.5	2.278	(1)
$\text{CF}_3\text{CBrF}_2$	Bromopentafluoroethane	198.94	---	-22	---	(2)
$\text{CF}_3\text{CF}_2\text{CBrF}_2$	1-Bromoheptafluoropropane	248.95	---	18	---	(4)

The monobromo compounds are prepared by the thermal bromination of the corresponding hydrogen-containing compounds (2):



or by special methods (1):



These compounds are of interest as anesthetics and fire extinguishers (3). Bromotrifluoromethane,  $\text{CBrF}_3$ , and dibromodifluoromethane,  $\text{CBr}_2\text{F}_2$ , have been found to be particularly effective where a nontoxic fire extinguisher is required.

**Iodofluorocarbons.** Two monoiodo fluoro compounds, iodotrifluoromethane,  $\text{CIF}_3$ , and iodopentafluoroethane,  $\text{CF}_3\text{CIF}_2$ , have been prepared. They are much more reactive than the fluorocarbons or the other halofluorocarbons, being decomposed by ultraviolet radiation and reacting with metals to form perfluoroalkylmetal iodides and metal perfluoroalkyls such as trifluoromethylmercuric iodide,  $\text{CF}_3\text{HgI}$  and bis(trifluoromethyl)mercury,  $(\text{CF}_3)_2\text{Hg}$  (1).

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### Benzotrifluoride.

Benzotrifluoride ( $\alpha, \alpha, \alpha$ -trifluorotoluene, phenylfluoroform),  $\text{C}_6\text{H}_5\text{CF}_3$ , formula weight 146.11, is a colorless, almost odorless compound; m.p.,  $-29.05^\circ\text{C}$ .; b.p.,  $103^\circ\text{C}$ .;  $d_4^{14}$ , 1.196; heat of vaporization, 10,460 cal./gram-mole; heat of fusion, 2,520 cal./gram-mole. Vapor pressure data and the Raman spectra have been determined (3,10). It was first prepared in yields of 60% in 1898 by the action of antimony trifluoride on benzotrichloride (13,14).

### CHEMICAL PROPERTIES

Benzotrifluoride is a very stable compound and can be distilled without any traces of decomposition. The  $\text{CF}_3$  group is very resistant to chemical reactions, as shown by the oxidation of the aminobenzotrifluorides with chromic oxide to trifluoroacetic acid. Nuclear substitution reactions take place predominantly in the meta position. Nitration at  $0^\circ\text{C}$ . gives 90% of 3-nitrobenzotrifluoride (7,16). Further nitration of this compound with fuming nitric and sulfuric acids gives the 3,5-dinitro compound (19). 3-Nitrobenzotrifluoride can be reduced to 3-aminobenzotrifluoride with any of the common reducing agents.

Chlorination (18) of benzotrifluoride with an antimony pentachloride catalyst at room temperature gives a 50% yield of the 3-chloro derivative. Chlorination in a sealed tube at room temperature gives a hexachloro(trifluoromethyl)cyclohexane (28). The introduction of chlorine atoms into the benzotrifluoride ring raises the boiling point approximately  $35^\circ\text{C}$ . for each chlorine atom that replaces a hydrogen atom. 3-Bromobenzotrifluoride is obtained in 73% yield by direct bromination (1). This compound and the iodo derivatives (formed from the amino compounds) will form Grignard reagents, but the chloro compounds do not.

Nitration of the 3-chloro derivative introduces a nitro group predominantly into the 6-position (20). Nitration of the 3-bromo compound gives a mixture that cannot be separated (4).

Benzotrifluoride is converted to benzoic acid when treated with aqueous hydrofluoric acid at  $100^\circ\text{C}$ . (14). In the presence of oxygen and anhydrous hydrogen fluo-

ride it goes to benzoyl fluoride (14). Hydrobromic acid in the presence of silica also converts the compound to benzoic acid (16). The  $\text{CF}_3$  group can be degraded to the acid with concentrated base (4) or 75% sulfuric acid (9), depending on what other groups are present on the ring.

Metalation with *n*-butyllithium takes place predominantly in the 2-position (8).

Aromatic compounds containing the  $\text{CF}_3$  group are somewhat toxic to frogs, and 3-aminobenzotrifluoride can be used as a narcotic (5).

#### PREPARATION

The commercial preparation (12,13) of benzotrifluoride consists in the reaction of 500 parts of benzotrichloride (see Vol. 3, p. 822) with 200 parts of hydrogen fluoride at  $0^\circ\text{C}$ . in a copper vessel fitted with a stirrer, an outlet tube, and an inlet tube reaching to the bottom. The hydrogen fluoride (anhydrous) is introduced over a period of 72 hours. During the reaction, the exit gases (hydrogen chloride and some hydrogen fluoride and benzotrifluoride) are collected in a well-cooled copper receiver. When the concentration of hydrogen fluoride in these gases rises to 70%, the reaction is stopped for the sake of economy. The relative amounts of the gases may be determined by using bead tests (silver nitrate and calcium chloride). The reaction mixture is combined with the contents of the receiver; the mixture is warmed to remove hydrogen fluoride; and sodium fluoride is added to remove the remnants of hydrogen fluoride. The crude product is isolated by filtration and distillation of the filtrate. About 300 parts of benzotrifluoride is obtained. The yields vary from 75 to 95%, depending on when the reaction is stopped. The final distillation fraction contains some chloro-fluorides, but these may be re-used in subsequent runs. This reaction can also be used to make chloro- or nitrobenzotrifluorides or bis(trifluoromethyl)benzenes by starting with the appropriately substituted benzotrichlorides. Benzotrifluoride can also be prepared by the vigorous reaction of benzotrichloride with antimony trifluoride (6,15-17,19,24).

#### USES

A number of nitro halo, nitro amino, and nitro methoxy derivatives have been prepared as dye intermediates (21). The presence of fluorine in dyes increases resistance to oxidation and helps prevent fading. The aminobenzotrifluorides can be diazotized and coupled with a variety of compounds to give useful dyes (27). The tetrachloro and dichloro derivatives have dielectric properties that make them useful in transformers (26). Hexachloro(trifluoromethyl)cyclohexane may be used as a heat-transfer liquid, a transformer fluid, or an insecticide (28). 4-Aminobenzotrifluoride forms a hard glassy resin at  $200^\circ\text{C}$ . with the evolution of hydrogen fluoride (4). 2-Hydroxy- and 4-hydroxybenzotrifluoride polymerize in a dilute base or with hydrogen fluoride (4). Substituted benzotrifluorides containing an ethylenic group (1) give hard polymers or may be copolymerized with butadiene to give rubbers that may be equal or superior to GR-S rubbers.

#### DERIVATIVES

**Aminobenzotrifluorides.** The amino derivatives (2-amino,  $b_{21}$   $73^\circ\text{C}$ .; 3-amino, b.p.  $187.5^\circ\text{C}$ .; 4-amino,  $b_{21}$   $74^\circ\text{C}$ .) are made by the reduction of the appropriate nitro compounds (9,17,23). 2-Aminobenzotrifluoride ( $\alpha,\alpha,\alpha$ -trifluoro-*o*-toluidine),  $\text{NH}_2\text{-C}_6\text{H}_4\text{CF}_3$ , formula weight 161.13, has been prepared from *N*-[*o*-(trichloromethyl)]phen-

yl]phthalimide,  $\text{OC}_6\text{H}_4\text{CO.NC}_6\text{H}_4\text{CCl}_3$ , by treatment with hydrogen fluoride at  $150^\circ\text{C}$ . (25). The desired compound is obtained by hydrolysis and steam distillation. The aminobenzotrifluorides can be oxidized to trifluoroacetic acid in yields of 50–60% (4,17). Acetylation of the 3-amino compound followed by nitration at  $0^\circ\text{C}$ . gives an 84% yield of 3-acetamido-6-nitrobenzotrifluoride ( $(\alpha^3, \alpha^3, \alpha^3\text{-trifluoro})\text{-4-nitro-}m\text{-aceto-toluide}$ ),  $\text{CF}_3\text{C}_6\text{H}_3(\text{NO}_2)\text{NHCCH}_3$  (9). The ortho isomer (3-acetamido-4-nitrobenzotrifluoride) is produced from the 3-amino derivative by the use of acetyl nitrate (9). From these compounds the 2- and 4-nitrobenzotrifluorides are obtained by hydrolysis and deamination. The hydroxybenzotrifluorides (4) are prepared from the aminobenzotrifluorides.

**Chlorobenzotrifluorides.** 2-Chlorobenzotrifluoride ( $\alpha, \alpha, \alpha\text{-trifluoro-}o\text{-chlorotoluene}$ ),  $\text{ClC}_6\text{H}_4\text{CF}_3$ , formula weight 182.58 (b.p.  $152.8^\circ\text{C}$ .), and 4-chlorobenzotrifluoride (b.p.  $139.3^\circ\text{C}$ .) can be made from the amino compounds by a Sandmeyer reaction or by treating chlorobenzotrichlorides with hydrogen fluoride or antimony trifluoride (2). 3-Chlorobenzotrifluoride (b.p.  $138.4^\circ\text{C}$ .) can be prepared by direct chlorination or from the 3-amino derivative (2,4,18) (see also p. 757).

**Nitrobenzotrifluorides.** 3-Nitrobenzotrifluoride ( $\alpha, \alpha, \alpha\text{-trifluoro-}m\text{-nitrotoluene}$ ),  $\text{NO}_2\text{C}_6\text{H}_4\text{CF}_3$  (b.p.  $102\text{--}103^\circ\text{C}$ .), is prepared by direct nitration, and the 2-nitro and 4-nitro compounds are prepared from the 3-amino derivative (see above). Amino-nitrobenzotrifluorides are made by nitration of the amino compounds or reduction of a dinitro compound with ammonium sulfide. Chloronitrobenzotrifluorides can be prepared by nitration of the chloro derivatives or from the nitro amino compounds by a Sandmeyer reaction (20,21,23).

The nitro compounds are low-melting solids, and the nitro amino compounds melt from  $60$  to  $130^\circ\text{C}$ ., while the halonitrobenzotrifluorides are usually liquids or low-melting solids.

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### Fluoroethanols.

The preparation of fluoroethanols was first reported by Swarts after 1900.

**2-Fluoroethanol** (ethylene fluorohydrin,  $\beta$ -fluoroethyl alcohol),  $\text{CH}_2\text{FCH}_2\text{OH}$ , formula weight 64.06, is a colorless liquid and has an odor like ethyl alcohol; m.p.,  $-26.45^\circ\text{C}$ .;  $b_{767}$ ,  $103.55^\circ\text{C}$ .;  $d_4^{20}$ , 1.1297;  $n_D^{18}$ , 1.13647; heat of combustion, 290.16 cal./gram-mole (12,13). It is a stable compound (does not decompose on distillation) and is completely miscible with water and many organic solvents. It does not corrode copper, Monel, nickel, or iron, although it is slightly acidic (will form salts with basic carbonates). It has a low flammability. The chemical properties of fluoroethanol are similar in many respects to those of ethylene chlorohydrin (2-chloroethanol) (see Vol. 3, p. 852). Although the fluorine atom does not react with metals, the hydroxyl group undergoes the usual reactions of that group (7). Oxidation gives fluoroacetic acid or fluoroacetaldehyde. With phosphorus tribromide, 2-fluoroethyl bromide is produced. Fluoroethanol has been reported to be relatively toxic (4,8).

The best method of preparation consists of the reaction of ethylene chlorohydrin with potassium fluoride at about  $170^\circ\text{C}$ . (6). The chlorohydrin is added dropwise to a suspension of the fluoride in a high-boiling solvent (ethylene glycol, diethylene glycol, glycerol, or mixtures of these) contained in a three-necked glass reactor or flask equipped with a mechanical stirrer, dropping funnel, and a Vigreux column. The crude material distills off during the reaction and is purified by fractionation. Small amounts of moisture do not affect the reaction appreciably. The yields are higher than when the reaction is run under pressure in the absence of solvent (after four hours in an autoclave at  $100^\circ$  the yield is 30% (7,8)). Slightly higher yields may be obtained with mercury fluoride, but potassium fluoride is more readily available and more economical.

Fluoroethanol has also been prepared by hydrolysis with dilute acid of 2-fluoroethyl acetate (obtained from 2-bromoethyl acetate and silver fluoride or mercuric fluoride (9,12,13) or from 2-chloroethyl acetate and potassium fluoride (4)) or by reaction of ethylene oxide in ether with dry hydrogen fluoride at  $100^\circ\text{C}$ . in a steel autoclave for six hours (40% yield) (7).

*2-Fluoroethyl acetate*,  $\text{CH}_2\text{FCH}_2\text{OOCCH}_3$ , formula weight 106.10 ( $b_{27}$   $45.5^\circ\text{C}$ .), has the odor of ethyl acetate and is easily saponified by dilute hydrochloric acid or dilute sulfuric acid (12,13).

**2,2-Difluoroethanol** (difluoroethanol),  $\text{CHF}_2\text{CH}_2\text{OH}$ , formula weight, 82.04, is a colorless liquid with the odor of ethyl alcohol; m.p.,  $28.2^\circ\text{C}$ .; b.p.,  $96^\circ\text{C}$ .;  $d_4^{17}$ ,

1.3084;  $n_D^{17}$ , 1.3320; heat of combustion, 245.3 cal./gram-mole. It is soluble in water and most organic solvents. Difluoroethanol is stable in air and can be distilled at atmospheric pressure. It is more acidic than fluoroethanol, since the acidity increases with the introduction of fluorine atoms. Difluoroethanol forms alcoholates (alkoxides) with sodium hydroxide, potassium carbonate, calcium oxide, and strontium oxide (10). An addition compound is formed with calcium chloride. Oxidation gives difluoroacetic acid (1). There is no reaction with silver nitrate. The methyl ether (b.p. 47°C.) is formed by the reaction of sodium methoxide with 2,2-difluoroethyl bromide. The ethyl ether is formed in a similar fashion and boils at 66.3–66.7°C. With phosphorus tribromide, difluoroethyl bromide is formed.

The compound is prepared by the reaction of difluoroethyl bromide or iodide with mercuric oxide or lead oxide in water at 140°C. in an autoclave (10). The yields are 92–93% after fractionation of the reaction products.

**2,2,2-Trifluoroethanol** (trifluoroethanol),  $\text{CF}_3\text{CH}_2\text{OH}$ , formula weight 98.04, is a colorless liquid; m.p.,  $-43.5^\circ\text{C}$ .; b.p.,  $74.5^\circ\text{C}$ .;  $d_4^{22}$ , 1.3739;  $d_4^0$ , 1.4106;  $n_D^{22}$ , 1.2907.

Trifluoroethanol is as acidic as phenol and is very stable. Trifluoroethanol undergoes the usual reactions of an alcohol and a phenol. The  $\text{CF}_3$  group is very stable. Like the other fluorinated alcohols, this compound is easily oxidized to trifluoroacetic acid, but the reaction cannot be stopped at the aldehyde. Trifluoroethyl ethyl ether (b.p.  $50.3^\circ\text{C}$ .) is formed from the sodium salt and ethyl bromide in dioxane. Attempts to prepare dry sodium trifluoroethoxide have resulted in violent explosions.

The best method of preparation consists in the reduction of trifluoroacetyl chloride (b.p.  $-27^\circ\text{C}$ .) with lithium aluminum hydride. The acyl chloride is admitted through an inlet tube into the bottom of a three-necked flask containing dry ether and equipped with a "dry ice" reflux condenser and a sealed stirrer. The system is kept under nitrogen. When the reaction is complete, the excess lithium aluminum hydride is decomposed with water, and the trifluoroethanol is obtained in 85% yield by fractionation. The alcohol has also been prepared in 76% yield by the reduction of trifluoroacetamide with platinum oxide at  $90^\circ\text{C}$ . for seven hours at 1500 p.s.i. (3). The preparation from the amide was first carried out by Swarts, who also reported the reduction of trifluoroacetic anhydride followed by saponification of the resulting ester, trifluoroethyl trifluoroacetate, to trifluoroethanol (14). The reduction of ethyl trifluoroacetate with copper chromite could not be accomplished. If trifluoroethyl chloride is treated with potassium acetate at  $225^\circ\text{C}$ . and the resulting ester saponified, trifluoroethanol is obtained (5). However, the yields are very sensitive to the reaction temperature.

Trifluoroethanol may be used as a refrigerant or copolymerized with other materials. The polymers resulting from the reaction of methacrylic acid chloride and trifluoroethanol with subsequent polymerization have low refractive indexes and high relative dispersions (15).

Trifluoroethyl ethyl ether may also be used as a refrigerant (13,14).

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JOHN F. NOBIS

### Fluoro Ethers and Amines.

**Trifluoroethyl ethyl ether**,  $\text{CF}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ , may be made from trifluoroethanol (see above).

**Perfluoroaliphatic Ethers and Perfluoroalkyl Tertiary Amines.** Numerous perfluoroaliphatic ethers and perfluoroalkyl tertiary amines have been prepared by the electrochemical fluorination process described by Simons *et al.* (1). These compounds are relatively inert, showing none of the typical reactions of ordinary aliphatic ethers

TABLE I. Physical Properties of Some Perfluoro Ethers and Tertiary Amines.<sup>a</sup>

Formula	B.p., °C.	$d_4^{25}$	$n_D^{25}$
A. Perfluoro Ethers			
$(\text{CF}_3)_2\text{O}$	-59	—	—
$(\text{C}_2\text{F}_5)_2\text{O}$	1	—	—
$\text{CF}_3\text{OCF}_2\text{CF}_2\text{OCF}_3$	43	—	—
$n\text{-C}_4\text{F}_9\text{OCF}_3$	36	1.59	1.241
$\text{C}_6\text{F}_{11}\text{OCF}_3^b$	82	1.75	1.275
$\text{C}_2\text{F}_5\text{OCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OC}_2\text{F}_5$	98	1.63	1.252
$(n\text{-C}_4\text{F}_9)_2\text{O}$	102	1.71	1.261
$(n\text{-C}_6\text{F}_{13})_2\text{O}$	139	1.78	1.268
$(n\text{-C}_8\text{F}_{17})_2\text{O}$	181	1.81	1.278
B. Perfluoro Tertiary Amines			
$(\text{CF}_3)_3\text{N}$	-11	—	—
$(\text{C}_2\text{F}_5)_2\text{NCF}_3$	45	—	1.253
$\text{C}_6\text{F}_{10}\text{NCF}_3^c$	66	1.76	1.275
$(\text{C}_2\text{F}_5)_3\text{N}$	71	1.73	1.262
$n\text{-C}_8\text{F}_{17}\text{N}(\text{C}_2\text{F}_5)_2$	93	1.77	1.270
$\text{C}_6\text{F}_{11}\text{N}(\text{CF}_3)_2^b$	111	1.82	1.284
$(n\text{-C}_8\text{F}_{17})_2\text{NC}_2\text{F}_5$	112	1.79	1.273
$(n\text{-C}_8\text{F}_{17})_3\text{N}$	130	1.82	1.279
$(\text{C}_2\text{F}_5)_2\text{NCF}_2\text{CF}_2\text{N}(\text{C}_2\text{F}_5)_2$	158	1.86	1.291
$(n\text{-C}_4\text{F}_9)_3\text{N}$	178	1.86	1.291
$(\text{C}_4\text{F}_9)_2\text{NCF}_2\text{CF}_2\text{N}(\text{C}_4\text{F}_9)_2$	250	1.90	1.308
$(n\text{-C}_6\text{F}_{13})_3\text{N}$	258	1.93	1.303

<sup>a</sup> Source: unpublished data, Minnesota Mining & Manufacturing Co., St. Paul, Minn.

<sup>b</sup>  $\text{C}_6\text{F}_{11}$  is the perfluorocyclohexyl radical.

<sup>c</sup> Perfluoro-1-methylpiperidine.

and amines. They do not form salts with acids or complexes with boron trifluoride, chemical properties characteristic of the basic oxygen or nitrogen atoms of the unsubstituted analogs. The substitution of fluorine for hydrogen has caused the loss of this basicity and consequent reactivity. The perfluoro ethers are unaffected by aqueous sodium hydroxide, hydrogen iodide, benzoyl chloride, or boron trifluoride. Similarly, the perfluoro amines are not attacked by methyl iodide, concentrated sulfuric acid, aqueous sodium hydroxide, aqueous or anhydrous hydrogen fluoride, or peroxides.

Being typical of completely fluorinated materials, these compounds are extraordinarily stable thermally. They can be heated to temperatures approaching red heat without decomposition. Several typical perfluoro ethers and amines are listed with some of their properties in Table I.

Both the perfluoro ethers and tertiary amines boil lower than their hydrocarbon analogs. Their high density, low refractive index, and low surface tension are characteristic of fully fluorinated compounds. They are highly soluble in other fluorocarbons and in benzotrifluoride, but are only moderately soluble or insoluble in alcohols, esters, ketones, or aromatic or aliphatic hydrocarbons. They are as nontoxic as fluorocarbons.

The dielectric properties of these materials are also extreme. Perfluorotri-*n*-butylamine, for example, has a dielectric constant of 1.75 and a loss factor considerably lower than 0.0005, both essentially constant over a frequency range of 0 to 10 megacycles.

These compounds are of potential value as heat-transfer mediums, hydraulic fluids, dielectric fluids, selective solvents, and inert reaction mediums.

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L. J. HALL AND W. H. PEARLSON

#### Trifluoroacetone.

Trifluoroacetone (1,1,1-trifluoro-2-propanone, trifluorodimethyl ketone),  $\text{CF}_3\text{C}(\text{O})\text{CH}_3$ , formula weight 110.05, is a sweet-smelling, colorless liquid; m.p.,  $-129^\circ\text{C}$ .; b.p.,  $21.9^\circ\text{C}$ .;  $d_4^{20}$ , 1.282; soly., 7.5 grams/100 grams water at  $20^\circ\text{C}$ ., 4 grams/100 grams water at  $50^\circ\text{C}$ .. Trifluoroacetone will undergo the usual reactions of a ketone without affecting the trifluoromethyl group (2). Reduction over Raney nickel at  $30$ – $100^\circ\text{C}$ . at  $50$ – $100$  atm. gives a 97% yield of trifluoroisopropyl alcohol (1,1,1-trifluoro-2-propanol) (b.p.  $77$ – $78^\circ\text{C}$ .) (4). Trifluoroacetone forms a bisulfite addition compound, a semicarbazone (m.p.  $127^\circ\text{C}$ .), and an oxime in a sealed tube (trans form, m.p.  $-1.5^\circ\text{C}$ ., b.p.  $102.5$ – $103^\circ\text{C}$ .).

Trifluoroacetone is prepared by hydrolysis of ethyl trifluoroacetoacetate or its sodium salt with dilute sulfuric acid (1,3). The keto ester is prepared by condensation of ethyl trifluoroacetate with ethyl acetate in the presence of sodium sand. Trifluoroacetone is also obtained along with a number of other fluorinated compounds from the vapor-phase fluorination of acetone at the surface of a copper gauze (1).

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JOHN F. NOBIS

## Fluorinated Acids.

### Monofluoroacetic Acid.

Monofluoroacetic acid,  $\text{CH}_2\text{FCOOH}$ , formula weight 78.04, is remarkable for its high toxicity to a great variety of warm-blooded animals, including man; m.p.,  $33^\circ\text{C}$ .; b.p.,  $165^\circ\text{C}$ .; heat of combustion at constant volume, 171.08 kg.-cal./gram-mole. This compound is produced commercially only in the form of its sodium salt, which is employed as an economic poison under the name "1080" (7). Monofluoroacetic acid has also been isolated in South Africa as a toxic principle of *Dichapetalum cymosum*, a plant more commonly called "ratsbane," which is used as a rodenticide.

Fluoroacetic acid and its derivatives are prepared from chloroacetic acid (see *Acetic acid*) or its derivatives by substitution of fluorine for the chlorine. Thallous fluoride and potassium fluoride are the reagents which have been most successfully employed. Substitution is generally carried out with the amide or esters of chloroacetic acid, since only with these derivatives are practical yields obtained.

*Sodium fluoroacetate*,  $\text{CH}_2\text{FCOONa}$ , formula weight 100.04, is a white powdery solid, m.p.  $200\text{--}202^\circ\text{C}$ ., with decomposition at temperatures slightly above the melting point. Its solubility at  $25^\circ\text{C}$ ., expressed as grams per 100 grams of solvent, has been found to be: water, 111; methanol, 5; ethyl alcohol, 1.4; acetone, 0.04; carbon tetrachloride, 0.004. The dry salt is mildly hygroscopic.

The basic raw materials used in the manufacture of 1080 are ethyl chloroacetate and potassium fluoride (6). The ester is lacrimatory, and consequently it is handled in a closed system of pipes throughout the process. It must be dry and contain no free acid, so the first process step is redistillation of the material. The potassium fluoride must be dry and finely pulverized—the finer the better. It is first oven-dried, then pulverized in a mill and stored in airtight containers until needed.

The two raw materials react in a well-stirred autoclave at  $200^\circ\text{C}$ . and a maximum pressure of 400 p.s.i. The reaction takes about eleven hours:



The ethyl fluoroacetate is distilled off and then allowed to react in an agitated tank with a methanol solution of sodium hydroxide:



The slurry containing the products is centrifuged. The cake of 1080 is then colored with purified Nigrosine (black dye) and dried in thin layers on stainless-steel pans, using a vacuum tray dryer. The product is screened and stored in drums for later packaging.

Great care must be taken to prevent the escape of the toxic ethyl fluoroacetate into the plant area. All of the liquids employed in manufacturing are handled in a closed system, which is welded wherever feasible. A check for tightness is made before each run.

Compound 1080, the one thousand and eightieth chemical tested for the Fish and Wildlife Service during World War II, is the most effective all-purpose rodenticide

known, since it has high toxicity to all species of rats tested, and has excellent acceptance and quick action. It is also said to be the only rodenticide which will give almost complete eradication of all rats in a given location. It is the only rat poison which has been successfully used in water solutions, where it is not subject to variations in potency, as it is in bait. There even seems to be a tendency for rats to prefer poisoned water to pure water, although this has never been definitely proved. In addition, rats apparently do not develop any significant tolerance to 1080 on ingestion of sublethal amounts, nor do they show significant reaction except after ingestion of lethal amounts. 1080 also has the advantages of absence of objectionable taste and odor, chemical stability, nonvolatility, and no toxicity or irritation to the skin of workers. Aqueous solutions are not absorbed through the unbroken skin (6). See also *Poisons, economic*.

Sodium fluoroacetate was originally developed for the National Defense Research Committee, which required 500 lb. Today, virtually the same equipment is used to supply the full commercial demand, which because of the efficiency of the product, is only about 10,000 lb. per year.

The following specifications have been set for 1080: active material, 90.0% minimum; inorganic fluoride, 1.0% maximum; total chlorine, 1.0% maximum; sodium hydroxide, 0.5% maximum; weight loss at 110°C., 1.5% maximum; screen analysis, 90% through a 35-mesh screen, minimum; insoluble matter in a 50% solution at 30°C., 0.2% maximum; iron in the insoluble matter, 0.01% maximum. Two grades of 1080 are commercially available, the uncolored 1080, and that containing  $0.5 \pm 0.1\%$  of Nigrosine.

A colorimetric microanalytical method has been reported for acetate and fluoroacetate (5). The analysis depends upon the formation of a basic lanthanum acetate, which absorbs iodine and gives a blue color. The method has been reported to be reliable for concentrations of fluoroacetate in the range 100–400  $\gamma$ . An analysis for total fluorine in fluoroacetic acid and derivatives may be made by fusion with sodium peroxide in a Parr bomb, followed by precipitation of lead chlorofluoride (4). The identification of monofluoroacetic acid as the barium salt has been described (3). The analysis is based upon the characteristic extinction of polarized light by the salt crystals.

Monofluoroacetic acid and its derivatives which can yield the fluoroacetate ion must be handled with extreme care, for they are extremely toxic to mammals, including man. The rodenticide 1080 should be used only in commercial and business establishments and on guarded municipal dumps by carefully instructed, reliable personnel competently supervised. It is not recommended for use in residential areas or for distribution in places where the public might be exposed to it. All carcasses of rodents destroyed with 1080 should be promptly burned. Such carcasses are poisonous to pets or other animals which might eat them.

*Methyl fluoroacetate*,  $\text{CH}_3\text{FCOOCH}_3$ , formula weight 92.07, like the ethyl ester, is very toxic; m.p.,  $-32^\circ\text{C}$ .; b.p.,  $104.5^\circ\text{C}$ .;  $d_4^{20}$ , 1.1744;  $n_D^{20}$ , 1.3679; soly., 15 grams/100 grams water (9).

*Ethyl fluoroacetate*,  $\text{CH}_3\text{FCOOC}_2\text{H}_5$ , formula weight 106.10, is used as an intermediate in the production of 1080; b.p.  $117\text{--}118^\circ\text{C}$ .;  $d_4^{20}$ , 1.0912; heat of combustion at constant volume, 502.55 kg.-cal./gram-mole (10). This compound is very toxic and dangerous to handle, because of its volatility.

$\alpha$ -*Fluoroacetamide*,  $\text{CH}_3\text{FCONH}_2$ , formula weight 77.06, melts at  $108^\circ\text{C}$ . (1). It has been reported to be useful as an insecticide.

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## Difluoroacetic Acid.

Difluoroacetic acid,  $\text{CHF}_2\text{COOH}$ , formula weight 96.02, is a colorless liquid with a sharp biting odor, that fumes in moist air; m.p.  $35^\circ\text{C}$ .; b.p.  $134.2^\circ\text{C}$ . It is soluble in water and many organic solvents, and is a strong acid. Difluoroacetic acid may be condensed with acetyl peroxide to yield tetrafluorosuccinic acid (9).

The free acid may be prepared by treating sodium difluoroacetate with sulfuric acid; by acidifying the solution obtained from the oxidation of 1,2-dichloro-3,3-difluoropropene ( $\text{CHF}_2\text{CCl:CHCl}$ ) and extracting the acid with several ether washes (2,6,8); and by oxidizing difluoroethanol with nitric acid or chromium trioxide (1,4). A recent patent describes the preparation from 2,4,6-tris(difluoromethyl)-*sym*-triazine by hydrolysis at  $50$ – $150^\circ\text{C}$ . in the presence of 0.1–10 parts of an acid or basic catalyst per part of triazine. An inert solvent such as dioxane may be used.

*Sodium difluoroacetate*,  $\text{CHF}_2\text{COONa}$ , formula weight 117.01, is a white odorless powder of bitter taste. It is deliquescent, freely soluble in water, and partly soluble in hot ethyl alcohol. It decomposes on strong heating.

A mixture of the sodium and potassium salts of difluoroacetic acid is obtained in accordance with the equation (2,6,8):



*Ethyl difluoroacetate*,  $\text{CHF}_2\text{COOC}_2\text{H}_5$ , formula weight 119.04, is a limpid, fragrant liquid; b.p.  $99.2^\circ\text{C}$ .;  $d^{17}_4$  1.18. It may be prepared by heating the acid or its sodium salt with sulfuric acid and ethyl alcohol. It can be produced in almost theoretical yield from the dilute difluoroacetic acid obtained from the oxidation of dichloro-3,3-difluoropropene. Ethyl difluoroacetate is formed in the vapor-phase fluorination of acetyl fluoride along with ethyl monofluoroacetate in the ratio of approximately 1:6 (3). The reactions of ethyl difluoroacetate are similar to those of ethyl trifluoroacetate (see p. 767).

*Vinyl difluoroacetate*,  $\text{CHF}_2\text{COOCH:CH}_2$ , formula weight 122.07, prepared by passing acetylene into difluoroacetic acid in the presence of catalysts (7), has been reported to polymerize into film-producing polymers of potential industrial importance.

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M. G. GERGEL AND MAX REVELISE

## Trifluoroacetic Acid.

Trifluoroacetic acid (perfluoroacetic acid),  $\text{CF}_3\text{COOH}$ , is a colorless liquid with a sharp biting odor; f.p.,  $-15.5^\circ\text{C}$ .; b.p.,  $72.4^\circ\text{C}$ .;  $d_4^{20}$ , 1.4890;  $n_D^{20}$ , 1.2850. It is freely soluble in water, ether, acetone, methanol, carbon tetrachloride, and benzene, and is very hygroscopic. Its constant-boiling mixture with water contains 79.4% trifluoroacetic acid and boils at  $105.5^\circ\text{C}$ . (12). Trifluoroacetic acid is a strong acid, comparable to hydrochloric acid, readily forming salts and esters (2). It is easily dehydrated with phosphorus pentoxide to yield the anhydride. The acid halide is produced in 79% yield with benzoyl chloride or bromide (3,14).

The free acid is available in anhydrous form, and its sodium salt as a free-flowing powder. The acid may be prepared easily in the laboratory from the salt. Other practicable laboratory preparations are the oxidation of benzotrifluoride (8) or its 3-amino derivative using a mixture of chromic acid and sulfuric acid; or the oxidation of 1,1,2-trichloro-3,3,3-trifluoropropene,  $\text{CF}_3\text{CCl}:\text{CCl}_2$ , with sodium hydroxide and potassium permanganate (15).

The free acid causes painful burns which are slow to heal; the vapors are extremely irritating. When pure, the acid is difficult to store due to its low surface tension with resulting tendency to creep through ground-glass closures. Glass bottles sealed with polystyrene caps containing a Teflon liner are satisfactory (12).

Sodium trifluoroacetate,  $\text{CF}_3\text{COONa}$ , is a white, odorless powder which absorbs moisture rapidly when exposed to air. It is very soluble in water and hot alcohol, slightly soluble in ether, and insoluble in benzene or chlorinated hydrocarbons. Unlike the monofluoroacetate, "1080," it is nontoxic. Electrolysis of sodium trifluoroacetate yields hexafluoroethane (10). *S*-Benzylthiuronium chloride reacts with sodium trifluoroacetate to form *S*-benzylthiuronium trifluoroacetate. Strong heating produces trifluoroacetyl fluoride by a pyrolysis which also produces carbon monoxide, carbon dioxide, trifluoroacetic anhydride, etc. (8). Sodium trifluoroacetate may prove an important intermediate in the preparation of other fluorinated compounds, and its physical and chemical properties suggest application in the preparation of herbicides, insecticides, and dyes (6).

Sodium trifluoroacetate is prepared by the oxidation of  $\text{CF}_3\text{CCl}:\text{CCl}_2$  (15), which yields the mixed sodium and potassium salts from which the acid, and subsequently the pure salt, can be obtained.

Ethyl trifluoroacetate,  $\text{CF}_3\text{COOC}_2\text{H}_5$ , is a liquid having a pleasant ester odor; b.p.  $61.7^\circ\text{C}$ .,  $d_4^{16}$  1.1953. It reacts with ammonia in anhydrous ether to give 99% yield of

trifluoroacetamide (1). This, when distilled with phosphorus pentoxide, gives trifluoroacetonitrile (1). Ethyl trifluoroacetate condenses with ethyl acetate in the presence of sodium ethoxide to produce ethyl trifluoroacetoacetate (4,9), which upon acid hydrolysis yields trifluoroacetone (see p. 763). When ethyl trifluoroacetate is condensed with acetone, the product is (trifluoroacetyl)acetone (1,1,1-trifluoro-2,4-pentanedione), and with trifluoroacetone it gives hexafluoroacetylacetone (3*H*,3*II*-hexafluoro-2,4-pentanedione). These acetylacetone derivatives form copper chelates which facilitate the separation of the products from the reaction mixture (4).

Ethyl trifluoroacetate is readily prepared from the acid or its sodium salt. Care must be taken to minimize losses by evaporation as the ester is extremely volatile. As prepared in the laboratory, the ester is often contaminated with water which affects the boiling point. With water and ethyl alcohol, a ternary mixture boiling at 54°C. is formed.

*Vinyl trifluoroacetate*,  $\text{CF}_3\text{COOCH}=\text{CH}_2$ . The polymerized ester has been suggested for use in lacquers, varnishes, adhesives for wood, metal, and glass, as wrapping material, and, if pigmented, as coating compounds (12,13,17).

*Trifluoroacetic anhydride*,  $(\text{CF}_3\text{CO})_2\text{O}$ , is a colorless liquid having a strong pungent odor; m.p.  $-65^\circ\text{C}$ ., b.p.  $40^\circ\text{C}$ . (11). It is easily prepared from trifluoroacetic acid by reaction with phosphorus pentoxide (8).

The anhydride was reported by Swarts (11) to yield trifluoroethanol (see p. 761) upon reduction with hydrogen under pressure, with platinum as catalyst.

The anhydride has been reported recently to be an excellent agent for conducting difficult esterifications. It does away with the necessity of a two-stage process and enables a rapid reaction to occur between the acid (by converting it to the more reactive anhydride) and the hydroxy compound under mild conditions (7).

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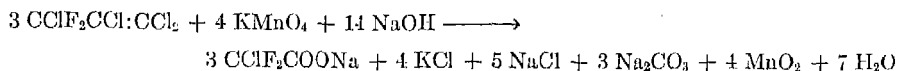
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M. G. GERGEL AND MAX REVELISE

**Difluoromono-chloroacetic Acid.**

Difluoromono-chloroacetic acid,  $\text{CClF}_2\text{COOH}$ , formula weight 130.50, is a colorless liquid fuming in moist air; m.p.  $22.9^\circ\text{C}$ ., b.p.  $121.5^\circ\text{C}$ . It is a strong acid, freely soluble in water, ether, and most organic solvents (2,3).

The preparation is similar to that of difluoroacetic acid through the salt (1):



*Ethyl difluoromono-chloroacetate* boils at  $97^\circ\text{C}$ . and has a density of 1.252 at  $23^\circ\text{C}$ . (2,3).

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M. G. GERGEL AND MAX REVELISE

**Heptafluorobutyric Acid.**

Heptafluorobutyric acid (perfluorobutyric acid),  $\text{CF}_3\text{CF}_2\text{CF}_2\text{COOH}$ , formula weight 214.05, is a colorless liquid having a sharp odor similar to butyric acid; f.p.,  $-17.5^\circ\text{C}$ .;  $b_{735}$ ,  $120.0^\circ\text{C}$ .;  $d_4^{25}$ , 1.541;  $n_D^{25}$ , 1.290. It is available as a product of the electrolytic reaction of hydrogen fluoride with butyric acid (1). Heptafluorobutyric acid is a very strong acid and is corrosive to the skin. It should be handled and stored with precautions similar to those applying to trifluoroacetic acid. It is very hygroscopic.

In the presence of pyridine and silver oxide, heptafluorobutyric acid decarboxylates giving heptafluoropropane,  $\text{C}_3\text{F}_7\text{H}$ , boiling from  $-17$  to  $-19^\circ\text{C}$ . With mineral acid catalysts, esters are obtained in excellent yields: *methyl heptafluorobutyrate*,  $b_{737}$   $79^\circ\text{C}$ .; *ethyl heptafluorobutyrate*,  $b_{744}$   $95^\circ\text{C}$ .,  $d_4^{20}$  1.394,  $n_D^{20}$  1.3032; *n-butyl heptafluorobutyrate*,  $b_{740}$   $132^\circ\text{C}$ . *Heptafluorobutyric anhydride*, m.p.  $-44$  to  $-46^\circ\text{C}$ .,  $b_{730}$   $107-107.5^\circ\text{C}$ .,  $d_4^{20}$  1.665,  $n_D^{20}$  1.285, is formed in 95% yield by the action of excess phosphorus pentoxide on the acid.

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M. G. GERGEL AND MAX REVELISE

**Perfluorocarboxylic Acids.**

See also "Trifluoroacetic acid" and "Heptafluorobutyric acid."

**PERFLUOROMONOCARBOXYLIC ACIDS**

Many of the perfluoromonocarboxylic acids have been prepared by the electrochemical fluorination of the corresponding carboxylic acids (9) involving the electrolysis of a solution of the organic acid in anhydrous hydrogen fluoride. The perfluoro acid fluoride is removed from the electrolytic cell as a gas or an insoluble liquid.



The physical properties of some straight-chain acids are listed in Table I (6). The boiling points are about 50°C. lower than those of the corresponding unsubstituted acids. Densities range from 1.5 to 1.8. Perfluoroacetic acid has a viscosity of 0.578 centistoke at 25°C., while perfluorobutyric acid has a viscosity of 1.622 at the same

TABLE I. Properties of Perfluoromonocarboxylic Acids.

Acid	Formula	B.p., °C.	d <sub>4</sub> <sup>20</sup>
Perfluoroacetic.....	CF <sub>3</sub> COOH	72.4	1.489
Perfluoropropionic.....	C <sub>2</sub> F <sub>5</sub> COOH	96	1.561
Perfluorobutyric.....	C <sub>3</sub> F <sub>7</sub> COOH	120	1.651
Perfluorovaleric.....	C <sub>4</sub> F <sub>9</sub> COOH	139	—
Perfluorocaproic.....	C <sub>5</sub> F <sub>11</sub> COOH	157	1.762
Perfluoroenanthic.....	C <sub>6</sub> F <sub>13</sub> COOH	175	1.792
Perfluorocaprylic.....	C <sub>7</sub> F <sub>15</sub> COOH	189	—
Perfluorocapric.....	C <sub>8</sub> F <sub>17</sub> COOH	218	—

temperature. The acids with fewer than eight carbon atoms are liquids at room temperature. Because of the extremely electronegative character of fluorine, these compounds are strong acids, which are essentially completely ionized in water solution. The acids exhibit the usual stability associated with fully fluorinated materials. They can be treated with strong alkali without hydrolysis of fluorine, and are not attacked by aqueous solutions of oxidizing or reducing agents. The higher members of the series have the property of decreasing the surface tension of aqueous solutions well below the point possible with any other type of surface-active agent. A 0.1% solution of perfluorocapric acid has a surface tension of only 19 dynes per centimeter at 30°C. (8).

The reactions of the perfluoro acids are, in general, similar to those of hydrocarbon acids. Salts are formed with the ease expected of strong acids. The heavy-metal salts are very hygroscopic. The metal salts are all water-soluble and much more soluble in organic solvents than the salts of the corresponding hydrocarbon acids. Esterification takes place readily with primary and secondary alcohols. Acid anhydrides can be prepared by distillation of the acids from phosphorus pentoxide, and halides can be prepared by standard procedures. The amides are readily prepared by ammonolysis of the acid halides, anhydrides, or esters and can be dehydrated to the corresponding nitriles (5).

Amines of the formula C<sub>n</sub>F<sub>2n+1</sub>CH<sub>2</sub>NH<sub>2</sub> can be prepared by the lithium aluminum hydride reduction of the corresponding amides or by hydrogenation of the nitriles. The analogous alcohols, C<sub>n</sub>F<sub>2n+1</sub>CH<sub>2</sub>OH, can be prepared by the high-pressure hydrogenation of the appropriate methyl or ethyl esters over a barium oxide stabilized chromite catalyst or by lithium aluminum hydride reduction of the acids or acid chlorides. Perfluoro aldehydes can be formed by modification of the above reductions (5). The derivatives of perfluorobutyric acid have been the most thoroughly studied (4).

#### PERFLUORODICARBOXYLIC ACIDS

The lower members of the series of perfluorodicarboxylic acids have been prepared and are stable compounds. They have been synthesized by oxidation of the appropriate chlorofluoroolefins as well as by electrochemical fluorination. Perfluoromalonic acid is an oxidation product of CH<sub>2</sub>:CHCF<sub>2</sub>CH:CH<sub>2</sub> (1). CF<sub>2</sub>.CF<sub>2</sub>.CCl:CCl has been

treated with basic potassium permanganate to yield perfluorosuccinic acid (3). Perfluoroglutaric and perfluoroadipic acids can be prepared by fluorination and subsequent oxidation of  $\text{CCl}_2\text{CCl}_2\text{CCl}_2\text{CCl}_2\text{CCl}_2$  and perchlorobenzene, respectively. The acids are recovered from the oxidation mixture by acidification with sulfuric acid and prolonged extraction with ether.

Table II lists some typical properties of some perfluorodicarboxylic acids.

TABLE II. Properties of Perfluorodicarboxylic Acids.

Acid	M.p., °C.	B.p., °C.	B.p. of diester, °C.	Ref
$\text{CF}_3(\text{COOH})_2$	—	—	58–59 <sub>9</sub> (methyl)	(1)
$(\text{CF}_2)_2(\text{COOH})_2$	87	150 <sub>15</sub>	89 <sub>15</sub> (ethyl)	(3)
$(\text{CF}_2)_3(\text{COOH})_2$	78–88	134–138 <sub>2</sub>	100 <sub>24</sub> (methyl)	(2)
$(\text{CF}_2)_4(\text{COOH})_2$	70–110 <sup>a</sup>	—	70–71 <sub>2,3</sub> (ethyl)	(7)

<sup>a</sup> Dihydrate.

These acids offer a convenient method for introducing a perfluoro radical into organic molecules. They are of potential interest in the preparation of polyamides and other fluorinated polymers.

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L. J. HALS AND W. H. PEARLSON

**FLUORITE**,  $\text{CaF}_2$ . See "Calcium fluoride" under *Fluorine compounds, inorganic*.

**FLUOROACETIC ACIDS**. See *Fluorine compounds, organic*.

**FLUOROCARBONS**. See *Fluorine compounds, organic*.

**FLUOROETHANOLS**. See *Fluorine compounds, organic*.

**FLUOROPHOSPHATES; FLUOROPHOSPHORIC ACIDS**. See "Phosphorus compounds" under *Fluorine compounds, inorganic*.

**FLUROSILANES**. See "Silicon compounds" under *Fluorine compounds, inorganic*.

**FLUORSPAR**,  $\text{CaF}_2$ . See "Calcium fluoride" under *Fluorine compounds, inorganic*.

**FLUOSILICATES; FLUOSILICIC ACID**,  $\text{H}_2\text{SiF}_6$ . See "Silicon compounds" under *Fluorine compounds, inorganic*.

**FLUOSULFONATES; FLUOSULFONIC ACID,  $\text{HSO}_3\text{F}$ .** See "Sulfur compounds" under *Fluorine compounds, inorganic*.

## FOAMS

Foams are dispersions in which air or other gases form the dispersed phase, and a liquid forms the continuous phase. However, such a system is usually called foam only if the concentration of the dispersed phase is high enough so that the system consists of gas bubbles separated from each other by thin layers of liquid. Shortening, for example, containing 20% air is hardly ever considered foam, whereas whipped cream containing 50% or more air by volume occasionally is considered foam. Obviously, the distinction is not always sharp. Foams are closely related to concentrated emulsions (creams), the only difference being that in the latter the dispersed phase is another liquid rather than a gas. See *Emulsions*.

**Condition for Formation and Stability of Foam.** In order to form foam, a gas has to be mixed with a liquid (1,4). This can be done, for instance, by chemical generation of gas in the liquid, or by mechanical introduction of the gas into the liquid, for example, by injection under the surface, by beating, by occlusion under a stream of liquid impinging on a liquid, etc. In all these cases, bubbles are formed in the liquid. These bubbles rise to the surface of the liquid at a rate that depends on their size and the viscosity of the liquid and the difference in density between gas and liquid. If every bubble that reaches the surface ruptures rapidly, the gas will leave the surface without forming a foam. In foamy liquids, the bubbles accumulate on top of each other before they rupture. The amount of foam at any given time is the result of the balance between the rate of foam formation and the rate of foam break.

Liquids consisting of a single pure chemical substance never foam. Aqueous solutions of surface-active agents and of high polymers are usually capable of foaming. To the former group belong soaps and organic detergents, to the latter proteins and vegetable gums. Certain nonaqueous solutions, for example, triethanolamine oleate in triethanolamine, or benzene in diethylene glycol, are also capable of foaming (30). See *Soap*; *Surface-active materials*.

The fact that solutions of surface-active agents are prominent among the foaming systems indicates the significance of surface tension for the stability of foam. Since foam is a system with an extremely large surface, it is obvious that low surface tension favors foam stability. However, low surface tension is not the only and not even the most important requirement for the stability of foam. It is more important that the liquid should have a reversible surface tension, or, expressed more exactly, mechanical extension of the surface should cause temporarily an increase in the surface tension, and a contraction of the surface should cause a decrease in the surface tension. Gibbs described this behavior as an elasticity of the film surrounding the gas bubbles. Therefore, as Bartsch found with the weakly foaming aqueous solutions of alcohols and acids, the maximum stability is usually obtained with solutions where the surface tension varies rapidly with the concentration and not where the tension has reached a minimum (3). Solutions of strongly surface-active agents, however, generally give more stable foams with increasing concentration, even when the minimum surface tension has been reached. The easy elimination of local inequalities of the surface tension of these solutions is probably due to their ability to replenish from the bulk phase the surface film when expanded, and allow the escape of the excess into the bulk phase when the surface film is compressed.

The eventual collapse of a foam is due to several factors. The breaking of an unstable emulsion is generally ascribed to the Brownian motion of the particles causing them to collide and merge with each other. Owing to the high viscosity of a foam, Brownian motion is hardly a factor in its collapse, just as it is hardly a factor in the collapse of a cream. Thinning of the film separating the bubbles precedes the collapse of the foam. There appears to be a critical thickness below which the film cannot be reduced without collapse occurring. The thinning proceeds by drainage due to gravity and by evaporation. The latter can be prevented by enclosure of the foam in a container. Mechanical shock, which distorts the film beyond its strength, accelerates the collapse, which, however, can occur spontaneously under the influence of the surface tension.

Plateau has shown that the viscosity of the film separating the bubbles often exhibits much higher values than the viscosity of the liquid in bulk form from which they are formed. He suggested that the ratio of the superficial viscosity to the surface tension of the solution determines the stability of the foam. Superficial viscosity can be measured by observing the oscillation of a disk suspended on a torsion wire and floating on the surface. However, the viscosity exhibited by the surface of most of the solutions forming stable foams is not a true Newtonian viscosity. The surface behaves rather like a plastic solid (18). As long as the shearing stress does not reach a critical value (yield value), the surface exhibits elasticity.

The drainage of the liquid increases with decreasing viscosity and, therefore, all other factors remaining constant, foam stability increases with viscosity of the solution. Increased temperature accelerates the decay of foam by reducing the viscosity and also by increasing the rate of evaporation. As the film separating the bubbles becomes thinner, surface viscosity rather than bulk viscosity will determine the rate of drainage.

**Adsorption and Foam Properties.** It is obvious that the difference in the behavior of the surface and of the bulk solution is due to the adsorption of the solutes on the surface. According to the theory of Gibbs, lowering the surface tension is connected with adsorption of surface-active solutes, and, according to the theories of Langmuir and Harkins, the adsorbed molecules are oriented. It is therefore to be assumed that both faces of the films separating the gas bubbles in the foams are covered by monomolecular layers of oriented molecules of the surface-active solutes. The thinnest soap film in its final stage has a thickness of approximately 50 Å., corresponding to the length of two soap molecules.

The fact that the ratio of the amount of the foaming compound to the amount of liquid is much higher in the foam than in the bulk of the solution, can be utilized for the concentration, removal, and identification of these compounds (foam analysis) (11, 20, 22, 23).

The stronger surface-active compound tends to displace the less active compound

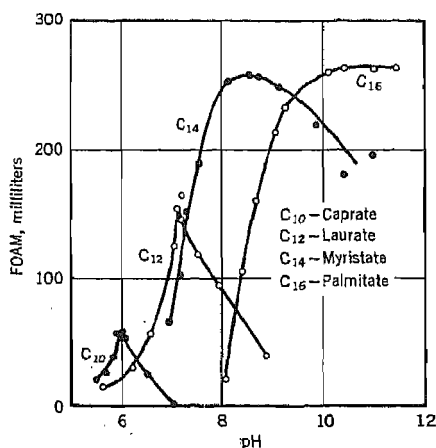


Fig. 1. Foam stability at 57°C. of 0.1% solutions of pure sodium salts of saturated fatty acids as a function of pH (21).

from the surface. The presence of small amounts of surface-active impurities, therefore, frequently has a tremendous effect on the stability of foam. The higher fatty acids, for example, are more surface active than their salts, the soaps. Soap solutions, depending upon the pH, contain varying amounts of undissociated fatty acids. This is reflected in the changes of the stability of the foam as a function of the changes in the pH of the solution (see Fig. 1). If the pH of the sodium caprate or sodium laurate solutions was raised to a point where the concentration of the undissociated fatty acid approached zero, the foam stability was also nearly zero. The strong adsorption of undissociated fatty acid in soap solution has been proved by Laing, who has shown that the solid in the froth obtained from neutral sodium oleate solutions contained about 0.7 molecule of oleic acid for each molecule of neutral soap (16,25). Likewise, a small amount of unsulfated lauryl alcohol stabilizes the foam of sodium lauryl sulfate (21a). In such a system, formation of foam gradually removes the surface-active impurity by selective adsorption.

**Testing of Foaming Ability.** Testing of solutions is carried out by using four types of methods of generating foam in a reproducible manner: (1) shaking the solution (by hand or mechanical means); (2) beating air into the solution (by rotating a stirrer or moving a perforated disk up and down) (8); (3) bubbling air or other gas through a column of the liquid (10); and (4) dropping the solution from a certain height (26). In each case, either the height of the foam or the amount of liquid contained in the foam is measured as a function of time. See also Vol. 2, p. 47.

One can use as a measure of foaminess either the average lifetime of the gas bubble or the average lifetime of the liquid in the foam. These can be related to the average lifetime of the foam by the concept of *relative foam density*, defined as the ratio of the liquid contained in the foam to the total foam volume, the latter being equal to the sum of volumes of gas and liquid (6).

It has been discovered experimentally that for many foams the rate of drainage of liquid obeys the equation:

$$V = V_0 e^{-kt}$$

where  $V$  is the volume of liquid in the foam at the time  $t$ ,  $V_0$  is the volume of liquid in the foam when  $t = 0$ , and  $k$  is a constant characteristic of each liquid from which the foam is formed. It is easily shown that the constant  $k$  is the reciprocal value of the average lifetime of the liquid in the foam (29). Bikerman suggested as a measure of foaminess the average lifetime of the bubble in the foam, determined by leading gas into a liquid until a constant height of foam was reached (5). The ratio of the height to the linear velocity of the gas represents the time during which any arbitrary volume of gas is present in the foam. Regardless of which method of measuring the foaminess is used, the significance of the results obtained is often limited to the exact conditions of foam formation.

While in many cases stability is the only property of foam that has been measured, there are a number of other characteristics likewise important. One of these is the bubble size or specific surface, which can be determined microscopically or by measuring the transmission of light (9). The mechanical properties of foam, which is a plastic body exhibiting viscosity, elasticity, and tensile strength, are also significant in many applications but are seldom measured.

### Industrial Applications

**Flotation of Minerals.** Flotation (*q.v.*) is essentially a mechanical method of separation, which utilizes the differences in the interfacial properties of particles. Owing to such differences, it is possible by interaction with organic reagents to render water-repellent the surface of particles to be floated, while simultaneously maintaining the surface of other particles hydrophilic (13). By causing the hydrophobic particles to become attached to air bubbles, they float in the separating medium, while the hydrophilic particles sink. The creation of air bubbles (frothing) is therefore an essential part of the flotation process. Since attachment of solid particles to the bubbles increases their stability considerably, frothers used in ore flotation are not necessarily good foaming agents by themselves.

**Fire fighting** (see also *Fire prevention and extinction*). The particular advantage of the application of foam in fire fighting is in combating gasoline fires because the application of water or any liquid with a specific gravity greater than gasoline results in the spread of fire by floating the burning liquid. The foam is generated by either a chemical reaction or mechanical agitation.

By chemical reaction, sodium bicarbonate is brought into contact with aluminum sulfate in the presence of a foam stabilizer, such as saponin, soap, glue, or a protein degradation product. The chemicals in aqueous solution may be stored in a closed compartmented container and the foam discharged under pressure. This is the form usually taken by hand extinguishers and small wheeled extinguishers. The chemicals in aqueous solution may be pumped into contact in fixed installations and the foam led to the required position. Finally, the solid chemicals can be introduced in dry form into a water stream and the foam delivered by the hose.

By mechanical agitation (mechanical foam or air foam), a positive-action rotating pump may be used to take water, air, and foam compound, and deliver the foam along the hose. Such apparatus is generally used for aircraft-crash fires, the pump being mounted on a vehicle carrying supplies of water and foam compound. A further method involves the use of a foam-making branch pipe. Particular requirements for foam stability in this case include the resistance to contact with gasoline and to exposure to high temperature. Clark has shown that foams generated with solutions of saponin, hydrolyzed keratin, or hydrolyzed blood in combination with ferrous sulfate meet these requirements (8). Partially hydrolyzed soybean protein is also being used (23,24).

**Detergency** (*q.v.*). Detergency has been always associated in popular concept with foaming. Lowering of interfacial tension is an essential requisite of detergency, and interfacial-active agents are usually foamers, soap being the outstanding example. The tendency of judging detergent efficiency by foaming ability may be explained, therefore, as a mere psychological consequence of this association. However, in many applications of detergents, foam has a definite function.

Foam acts as a lubricant, mechanically facilitating the application of the detergent solution. This is true not only for the cleaning of the human body and hair, but also for the scouring of textiles. In the latter case, the viscoelastic lather protects the fibers as a buffer against damage by friction. The semisolid or plastic nature of lather allows the application of the detergent solution to confined spaces by minimizing its flow. This is an important factor in the use of hair shampoo and especially of rug shampoo. In location cleaning, the wetting of the back of the rug has to be kept at a minimum

The operation consists of the application of a detergent solution, in the form of foam, with a brushing machine, and removal of the soil-laden foam with a power vacuum (17). Another outstanding example is the application of lather in shaving. Foam serves frequently as an indicator for the presence of detergents at a minimum level. Foam removes dirt from the cleaning solution by flotation.

**Formation of Porous Bodies.** Under certain conditions, it is possible to solidify permanently the films separating the bubbles, and, thus, to produce porous bodies. This method is being used in the culinary arts (meringue) and in the manufacture of so-called foam rubber, lightweight concrete, etc.

**Miscellaneous Applications.** Frequently, foam serves apparently only to satisfy a traditional requirement or a preference, as in the case of bubble bath and beer. The foaming agents in beer are the proteins, the hop resins, and the carbohydrates (14,31). In wines, foam formation sometimes occurs but is considered objectionable (2).

### Foam Prevention

In many industrial operations, the formation of foam is regarded as obnoxious. It causes losses by overflow of the expanded liquid; it produces variations in the weights of goods filled into containers; and it makes coatings porous. Excessive formation of foam can be only the result of continuous introduction of gas into liquid. In some cases, this can be avoided and, in other cases, mechanical devices (for example, overheating the foam above the surface of the liquid or pulsating streams of gas above the liquid) suffice to control foaming. In most cases, however, the liquid must be treated so that the bubbles break the moment they reach the surface. This is the case in the manufacture of paper and glue, the production of yeast and penicillin, the printing of textiles, the dehydration of crude oils, and the operation of steam boilers and of automotive radiators.

Quinke was the first to describe the destruction of foam by chemical means, namely, the effect of ether vapor on soap foam. Later, vegetable, animal, and mineral oils found industrial application in combating foam. The chemical industry offers today a great number of antifoaming agents representing a wide variety of substances. The effect of antifoaming agents is frequently a specific one in that, for combating a particular type of foam, a particular type of substance can be used with advantage.

According to Ross, 2-ethylhexanol (frequently referred to as "octyl alcohol") is widely used in beet-sugar production, paper manufacture, textile printing, glue spreading, and as a general defoamer for special solutions (28). Diisobutylcarbinol (2,6-dimethyl-4-heptanol) is usually equally effective and is applied in the neutralization of waste sulfuric acid with calcium carbonate, the paper industry, printing inks, and glues.

The foaming in steam boilers, particularly locomotive boilers, is attributed to the accumulation of salts. Carryover occurs when a critical concentration is reached. Condition of the heating surface where the bubble originates appears to be also an important factor (12,15). Until recently, castor oil was used for the prevention of foaming in boilers. Its usefulness was limited by its ready saponification. More effective than castor oil are the higher polymerized glycols and their ethers marketed under the name Ucon Brand Fluid. The higher fatty acid amides are also very effective, particularly the polyamides, such as *N,N'*-distearoylethylenediamide (33). These are sufficiently stable against hydrolysis. Used mostly in combination with tannin, the

polyamides permit the attainment of dissolved-solids concentrations of approximately 1-2% or higher before carryover due to foam occurs (32,36,37,40,41,42,44,46).

Other antifoaming agents for various applications are fatty acids and fatty acid esters (34,38), pine oil, alkyl lactates, higher ethers such as 2-(di-*tert*-amylphenoxy)-ethanol (39,43), organic phosphates, and metallic soaps. Specific advantage of the naturally occurring fats and other edible fatty acid esters, such as the sorbitan esters (Spans), is that they can be used in the food industry.

The most effective and versatile agents are among the silicones (*q.v.*) (DC Antifoam A and Anti-Foam 81066). Concentrations in the range of 20-200 p.p.m. in most aqueous systems, and in some cases less than 1 p.p.m., are claimed to be effective.

Mixtures of the type of glycerol with sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT) have been found to be foam inhibitors for aeronautical lubricating oil (19).

Most foam-inhibiting agents are water-insoluble and are to be applied in emulsified form. It is assumed that they act by spreading on the surface and, therefore, displacing or covering the surface layer formed by the foaming agent. Surface films formed by the foam-inhibiting compounds lack the elasticity required for the formation of stable foams.

It appears to be generally true that the foam-inhibiting compounds have a high spreading coefficient,  $S$ :

$$S = \gamma_F - \gamma_A - \gamma_{AF}$$

where  $\gamma_F$  and  $\gamma_A$  are surface tensions of foaming liquid and antifoam, respectively, and  $\gamma_{AF}$  their interfacial tension.

Ross and McBain found that in nonaqueous foaming systems an additive need not be insoluble to be an effective foam inhibitor or foam breaker (30). They conclude that the chemical inhibition of foaming may be accomplished by more than a single mechanism.

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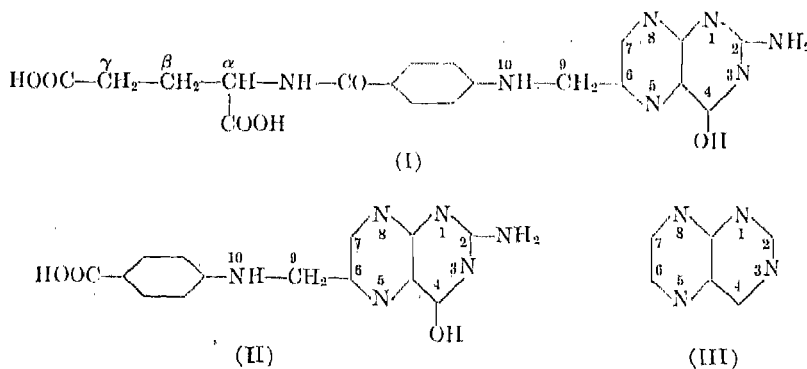


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## FOLIC ACID

The name folic acid is commonly applied to pteroylglutamic acid (PGA), a member of the vitamin B complex (see *Vitamins*), used in the treatment of certain anemias and other nutritional disturbances resulting from dietary deficiencies (see also *Antianemia preparations*). Before its chemical identification, pteroylglutamic acid was recognized



and measured by means of this biological activity. Various names, including vitamin M, factor U, vitamin B<sub>9</sub>, yeast norite eluate factor, folic acid, and *Lactobacillus casei* factor, were used to designate this biological activity (21), which is shared by several naturally occurring compounds; these names are, therefore, nonspecific.

Pteroylglutamic acid (I) (*N*-{*p*-[(2-amino-4-hydroxy-6-pteridylmethyl)amino]benzoyl}glutamic acid (*C.A.*)) (1) is a yellow crystalline compound, whose pteroyl radical (from pteric acid (II)) is a 6-(*N*-(*p*-amino)benzoyl) derivative of pteridine (III) (pyrimido[4,5-*b*]pyrazine, *R.I.* 959). See also "Pterins" under *Heterocyclic compounds*.

### Physical and Chemical Properties

Pteroylglutamic acid, crystallized from water, appears as yellow, spear-shaped leaflets. On heating, it does not melt but darkens and chars at around 250°C. (35);  $[\alpha]_D^{20}$ , +16° (in 0.1 *N* sodium hydroxide solution; concn. 0.76 gram/100 ml.) (53). It is soluble in water as the free acid to the extent of 1 mg./100 ml. at 0°C., and over 50 mg./100 ml. at 100°C. (48). Pteroylglutamic acid is practically insoluble in most common organic solvents, but is slightly soluble in acetic acid (35). The disodium salt has a solubility of over 1.5 grams/100 ml. The alkali metal and alkaline earth salts involving the enolic hydroxyl as well as the two carboxyl groups are quite soluble in water. The zinc, lead, and silver salts are quite insoluble (35,48,74).

Although drying of pteroylglutamic acid at moderate temperatures and atmospheric pressure leaves an amount of water corresponding roughly to a dihydrate, and samples dried at 145°C. in high vacuum are hygroscopic, optical crystallographic studies indicate that it is not a true hydrate (35).

Pteroylglutamic acid has characteristic ultraviolet absorption spectra (1,3,35,52). In 0.1 *N* sodium hydroxide solution, it exhibits maxima at 256, 282, and 365  $\mu$  and corresponding *E* (1% 1 cm.) values of 585, 570, and 206. At pH 11, maxima were obtained at the same points but with absorption coefficients that were slightly higher; 603, 600, and 213 at wave lengths of 256, 282, and 365  $\mu$ , respectively.

Dihydropteroylglutamic acid is formed by catalytic hydrogenation in the pyrazine ring of pteroylglutamic acid in dilute alkali and in glacial acetic acid over platinum; 2 moles of hydrogen are consumed. The dihydro form is readily oxidized again by air to pteroylglutamic acid (32). Reduction with zinc and acid leads to cleavage at the 9,10-linkage with formation of *N*-(*p*-aminobenzoyl)glutamic acid; this reaction is utilized in the chemical assay. Pteroylglutamic acid in alkaline solutions is oxidized in the presence of oxygen with cleavage (48). In dilute solutions, it is likewise cleaved with sulfurous acid (19), as it is in dilute neutral (46) or alkaline (3) solutions in daylight.

With nitrous acid in the cold, pteroylglutamic acid gives *N*<sup>10</sup>-nitropteroylglutamic acid (7), having biological activity apparently equal to the parent vitamin in the nutrition of the chick and *Streptococcus faecalis* R. Heating pteroylglutamic acid with formic acid and acetic anhydride gives a formylpteroylglutamic acid (10).

### Chemical Assay

Pteroylglutamic acid may be determined chemically by the method of Hutchings and co-workers (18). This method involves the cleaving of the molecule by acid reduction to yield a pteridine and *N*-(*p*-aminobenzoyl)glutamic acid, the latter then

being measured by the method of Bratton and Marshall by diazotization and coupling with *N*-(1-naphthyl)ethylenediamine. A suitable photoelectric colorimeter or spectrophotometer is used to measure the intensity of the resulting color at 550 m $\mu$ .

The reducing agent employed is zinc dust in the presence of 0.5 *N* hydrochloric acid. A low concentration of gelatin (0.005%) is included in the reaction mixture to protect the resulting amine from degradation.

The method has been adopted by N.N.R.—1949 (30), and has been accepted in virtually unchanged form for use in U.S.P. XIV (51). A modification has been proposed in which zinc amalgam is used as the reducing agent, the mixture being shaken mechanically for 30 minutes (18).

The chemical method is used for the standardization of commercial samples of pteroylglutamic acid, and in the assay of simple pharmaceutical mixtures of pteroylglutamic acid with inert solvents or diluents. While the original authors found the method satisfactory for the determination of pteroylglutamic acid in concentrates derived from natural sources when the content of the active compound was 5% or greater, only recently has the application of the method to pharmaceutical combinations of pteroylglutamic acid with other drugs been subjected to study (20,33).

Pteroylglutamic acid in natural materials is determined by microbiological assay (47).

### Occurrence

In common with the other B-complex vitamins, pteroylglutamic acid is widely distributed in biological materials, but in concentrations of only a few parts per million (9). It occurs principally both free and in the form of "conjugates," in which the pteroylglutamic acid molecule is attached to additional glutamic acid groupings. Conjugates with three (17) and seven glutamic acid groups (36,36a), respectively, have been isolated. *N*<sup>10</sup>-Formylpterioic acid or rhizopterin, a glutamic acid-free product closely related to pteroylglutamic acid, but apparently having biological activity confined to certain microorganisms such as *Streptococcus faecalis* R., has been isolated and synthesized (23,37,38,55). Good dietary sources of pteroylglutamic acid include liver, green leaves, yeast, and egg yolk. The cereal grains and, in general, fruits are poor sources (1,24). Prepared synthetically, pteroylglutamic acid is available commercially either as the crystalline substance for pharmaceutical purposes or as a crude concentrate for use in animal feeds.

### Preparation

Although isolation or partial purification of naturally occurring pteroylglutamic acid and its conjugates (12,14,15,17,26,27,31,34,35,40,44,45,48,49,59) served as a source of material for some biological work and for degradation studies, adequate supplies in commercial quantity were available only after the first synthesis of pteroylglutamic acid (1). Of the various synthetic methods tried, the most practical procedure depends to some extent on the starting materials available.

The first method of synthesis, and probably one of the most widely published, involved the simultaneous reaction of 2,4,5-triamino-6-hydroxypyrimidine, *N*-(*p*-aminobenzoyl)glutamic acid, and 2,3-dibromopropionaldehyde in aqueous solution (1,52). Following this, many related synthetic methods have been published in which different three-carbon systems are used in place of 2,3-dibromopropionaldehyde.

Examples of these three-carbon intermediates are derivatives of acrolein (2,64,65, 81,82), pyruvaldehyde (63,69), propionaldehyde (22,68), acetone (54,67,76), propylene oxide (77), propene (75), and  $\beta$ -formylacrylic acid (66).

Another method involves formation of a 2-amino-4-hydroxy-6-methylpteridine with a suitable substituent in the 6-methyl group for reaction with the *N*-(*p*-aminobenzoyl)glutamic acid. Examples of these substituted 6-methyl groups are:  $-\text{CH}_2\text{Cl}$  (60),  $-\text{CHO}$  (53,61,62),  $-\text{CH}_2\text{OH}$  (82,83), brominated methyl (6), and  $-(\text{CH}_2\text{N}-\text{C}_6\text{H}_5)^+\text{I}^-$  (13,78). Pteroylglutamic acid has also been prepared by the reaction of pteroyl chloride and glutamic ester (57), or a 2,10-diacylpteroyl chloride with glutamic acid esters, followed by hydrolysis (58). Still another type of synthesis involves the ammonolysis of a 2-alkylmercapto analog of pteroylglutamic acid (59).

The purification of folic acid obtained by almost all of the processes mentioned is difficult. The reactions lead to formation of polymerization products, position isomers, and oxidation products, as well as unreacted intermediates. Many of these impurities contain the pteridine nucleus, and show tendencies to coprecipitate with folic acid.

Early purification methods were modifications of some of the tedious processes used in isolation of natural concentrates, such as adsorption on charcoal, or removal of impurities by extraction of aqueous solutions of pteroylglutamic acid with solvents. Later improvements involve dissolving crude reaction products in aqueous alkali, adding a water-soluble alkaline earth salt such as barium chloride, and adding alcohol. This precipitates some of the impurities, part of which are probably 6- or 7-substituted 2-amino-4-hydroxypteridines (pterins). After removal of the alkaline earth, the solution may be acidified to pH 3-4 to precipitate pteroylglutamic acid (70). Certain insoluble salts, such as the zinc salt (73,74), are useful in isolating the pteroylglutamic acid from solutions, effecting some purification; recrystallization of the magnesium salt is also helpful (80). Dissolving the crude material in aqueous alkali and adjusting the pH to about 7 precipitates some neutral pterin-like materials (71). The isolation at pH 3-4 of the free pteroylglutamic acid or precipitation by dilution of solutions in strong acids brings about some purification (79). Frequently it is necessary to repeat one or more of the purification steps to obtain satisfactory materials. A final purification often can be effected by recrystallization from water. Experience indicates that preparations of pteroylglutamic acid may in the course of manufacture be dried without decomposition at temperatures up to 50°C. at ordinary pressure.

### Pharmaceutical Preparations

Folic acid (U.S.P. XIV) is supplied as a yellowish-orange powder containing an equilibrium quantity of moisture (51). The loss on drying should not exceed 10% at 70-75°C. and 15 mm. Hg; the content of pteroylglutamic acid should be not less than 94% on the anhydrous basis. The residue on ignition of 100 mg. should be negligible.

Pteroylglutamic acid is very slightly soluble in water but is soluble in solutions of the alkalis. Although air oxidative cleavage of these alkaline solutions can be brought about, the inclusion of an inert atmosphere in such preparations as ampuls is not necessary. On prolonged standing, they do not undergo a significant loss in pteroylglutamic acid content. For ampul use, a parenteral grade of pteroylglutamic acid is supplied. The solutions may be sterilized by autoclaving at a pressure of 15 p.s.i. in the usual manner.

Pteroylglutamic acid has been successfully compounded by known procedures in dry preparations, for example, tablets and capsules, both alone and in combination with other medicinal agents, such as iron salts, liver powder and extracts, and various factors of the vitamin B complex. In products of this type, a slight excess of pteroylglutamic acid is usually found sufficient to insure the maintenance of labeled potency. Pteroylglutamic acid combinations in the form of an oily suspension in soft gelatin capsules are also widely used and exhibit good stability.

Pteroylglutamic acid in solutions containing other B-complex vitamins presents a problem in stability that has been overcome with a considerable degree of success by careful attention to the following points: (1) Pteroylglutamic acid, when alone in solution, is chemically stable over a broad range of pH, for example, between 4 and 9. However, below pH 7 the solubility is so low that it is not practical to compound liquid preparations in the acid range. (2) Liver extracts and iron salts do not affect the stability of pteroylglutamic acid solutions materially. However, the presence of liver extracts permits the preparation of permanent solutions at lower pH levels than otherwise possible. (3) Certain factors of the B-complex and also vitamin C have a deleterious effect on pteroylglutamic acid. Riboflavin (vitamin B<sub>2</sub>) is the worst offender in this regard. This incompatibility can be overcome in considerable part by the incorporation of approximately 70% of sugars such as sucrose or corn sirup in the product. The mechanism of this stabilization is not known. (4) In the case of many formulas, the pteroylglutamic acid is more stable when incorporated directly as a powder than when it is first dissolved with the aid of alkali and the solution is added in the course of preparation.

### Biological Functions and Applications

A dietary deficiency of pteroylglutamic acid produces macrocytic anemia in various species of animals. The deficiency has been studied in human subjects during pregnancy and is characterized by abnormally low red- and white-cell counts and blood-hemoglobin levels, enlarged red cells, and a megaloblastic bone-marrow pattern resembling that seen in pernicious anemia in relapse. Hydrochloric acid is present in the gastric juice. The patient is weak and may have a sore tongue. The signs and symptoms disappear when pteroylglutamic acid, 5–20 mg. daily, is administered parenterally by mouth (28). See also *Antianemia preparations*.

In pernicious anemia, pteroylglutamic acid produces a hemopoietic response but is ineffective against the neurological changes that often accompany this disease and respond to liver extract or vitamin B<sub>12</sub> unless the lesions have progressed too far. The use of pteroylglutamic acid in pernicious anemia is therefore an adjuvant to liver extract or other sources of vitamin B<sub>12</sub> (30). Pteroylglutamic acid is used in the treatment of sprue in relieving the anemia and to some extent the diarrhea that occur in this disease (8). Certain authors have divided the megaloblastic anemias into two groups, one associated with dietary deficiency, which responds to folic acid (25), the other accompanied by gastric atrophy and neurological lesions, which responds to sources of vitamin B<sub>12</sub> (21). The simultaneous administration of pteroylglutamic acid and vitamin B<sub>12</sub> will serve to control both classes of these anemias.

Pteroylglutamic acid is used to some extent in animal nutrition as a feed supplement where a dietary deficiency of folic acid is encountered. Fur-bearing animals such as mink and foxes appear to be unusually prone to such a deficiency, especially during pregnancy (39). Pteroylglutamic acid, like the other B-vitamins, is a sub-

stance of low toxicity (11). It is used clinically as an ingredient of antianemia preparations and polyvitamin formulas.

A relation between pteroylglutamic acid and nucleic acid metabolism is shown by the interchangeability of thymine (5-methyluracil) and pteroylglutamic acid as growth factors for certain lactic acid bacteria (43). Pteroylglutamic acid appears also to be related biologically to ascorbic acid, as shown by similar effects of the two substances in reducing the urinary excretion of certain tyrosine derivatives in scorbutic guinea pigs (56).

### Derivatives and Analogs

The great interest in the effects of structural variations of pteroylglutamic acid on its biological properties has led to the preparation of at least one hundred analogs. These variations in most cases fall into the following general classifications: (1) Changes in the substituents in the 2- and 4-positions; (2) replacement of the pteridine moiety by another cyclic system; (3) change of or substitution in the 9,10-positions; (4) replacement of glutamic acid by other amino acids or peptides; or (5) replacement of the *p*-aminobenzoyl group by position isomers or the sulfanilic acid radical.

One of the most important of the analogs is called 4-aminopteroylglutamic acid (*N*-{*p*-[(2,4-diamino-6-pteridylmethyl)amino]benzoyl}glutamic acid (*C.A.*), Amino-pterin), in which the 4-hydroxy group is replaced by an amino group. It is prepared by a process similar to that used for pteroylglutamic acid, except that 2,4,5,6-tetraaminopyrimidine is used in place of 2,4,5-triamino-6-hydroxypyrimidine (42). 4-Aminopteroylglutamic acid is a powerful antagonist for pteroylglutamic acid, and as such has been studied extensively and has shown some promise for treatment of certain leukemias (50).

4-Amino-*N*<sup>10</sup>-methylpteroylglutamic acid (Amethopterin) (41) and 4-amino-pteroylaspartic acid (Amino-An-Fol) (16) are somewhat less potent as pteroylglutamic acid antagonists, but have been used in studies similar to those with 4-aminopteroylglutamic acid (50). These are prepared by a method very similar to that used for 4-aminopteroylglutamic acid, using instead of *N*-(*p*-aminobenzoyl)glutamic acid the required *N*-(*p*-(methylamino)benzoyl)glutamic acid or *N*-(*p*-aminobenzoyl)aspartic acid.

Pteroyl- $\gamma,\gamma$ -diglutamylglutamic acid, (also known as the fermentation *Lactobacillus casei* factor, pteroyltriglutamic acid, and Teropterin), has been synthesized by methods similar to those used for pteroylglutamic acid, except that *N*-(*p*-aminobenzoyl)- $\gamma,\gamma$ -diglutamylglutamic acid is used in place of *N*-(*p*-aminobenzoyl)glutamic acid (4,5). Pteroyltriglutamic acid and pteroyl- $\alpha$ -glutamylglutamic acid (29) (pteroyldiglutamic acid, Diopterin) have been studied in the treatment of neoplastic diseases (50). Pteroyltriglutamic acid is 2-4% as active as pteroylglutamic acid when assayed with *Streptococcus faecalis* R., and on a molar basis is as active as pteroylglutamic acid when assayed with *L. casei*. It appears to be as effective as pteroylglutamic acid in alleviating pteroylglutamic acid deficiencies in birds and mammals (21).

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**FOLLICULAR HORMONE.** See "Sex hormones" under *Hormones*.

## FOOD AND FOOD PROCESSING

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Food or foodstuff is a general term used to designate what is consumed by human beings for the sustenance of life. The immediate reason for eating is hunger and the most immediate result of eating is the disappearance of the hunger sensation and its more direct manifestation, appetite. Hunger and appetite both may be regarded as results of the human body's need for food.



Food eaten has several functions in the body. It provides a source of energy to maintain the body temperature above the sharply defined minimum temperature below which life ceases. In addition, it provides building materials of all sorts for the production and replacement of the innumerable types of tissues, bones, body fluids, etc. Finally, certain food components like vitamins afford proper control of various processes required for the normal functioning of the body.

The history of food is the history of the human race. Following prehistoric times, when man was dependent upon incidental and irregular food supplies, there developed various primitive agricultural pursuits, especially the growing of cereal grains and the raising of animals for slaughter. The formation of cities resulted in the development of increasingly organized food production, handling, and storage. As cultures developed, additional foods of various origins and degrees of sophistication were provided, but until about a hundred years ago efforts toward improving food supplies were much inhibited by unsuitable methods of handling and slow transport.

There are few matters in which tradition plays such a dominant role as in food habits. The diet of many peoples today is essentially what it was hundreds of years ago, and many dishes staple now were well known in Biblical times. It was only with the advent of efficient methods of influencing people (mainly by education and advertising) that new foods and food habits could be introduced within the span of a few years.

For some time, it was believed that an abundant and varied diet would provide all the needs of the body, but it is now known that this is often not the case. Complications are at times introduced by the extensive use of manufactured and processed foods where undesirable food habits might easily develop because of convenience or economy. While most animals have retained the ability to make a choice of foods needed for their bodies, this faculty has been to a great extent lost by man. The choice of food with human beings is governed by both physiological and psychological factors, but it is not quite clear to what extent one or the other will dominate under different circumstances (13). Systematic large-scale tests, during and since World War II, of food preferences and of voluntary food intake have supplied many interesting and important leads on this subject.

Ingested food has to be digested and absorbed before the body can make use of it. Certain approximations of the value of various foods in supplying the body's needs are now commonly used in evaluating the efficiency of various diets. The science dealing with the formulation of adequate diets is dietetics, and the ultimate utility of a food is assessed by the science of nutrition.

### Classification of Foods

The great variety of foods produced and consumed by man can be classified along several lines, none of which seems to be entirely satisfactory. The following list gives most of the important foods, including beverages and food components:

- (1) Water.
- (2) Salt and other inorganic compounds, including trace elements.
- (3) Cereals and cereal products.
- (4) Fruits, vegetables, mushrooms, nuts. This group of plant foods includes tubers, bulbs, roots, stems, leaves, shoots, flowers, fruits, and other structures, as well as fruit and vegetable juices.

- (5) Sugars and starches. These are predominantly manufactured products.
- (6) Fats and oils. These include oilseeds, animal fats, whale oil, etc.
- (7) Meats and meat products, including poultry.
- (8) Dairy products and eggs. Milk, butter, cheese, etc.
- (9) Sea food. Mostly fish and shellfish.
- (10) Beverages. Tea, coffee, maté, cocoa, etc.
- (11) Alcoholic and synthetic carbonated drinks. Beer, wine, gin, brandy, rum, whisky, liquors, cordials, squashes, soda drinks, etc.
- (12) Spices, relishes, essential oils. Many of these are manufactured products.
- (13) Compound foods made up of various major ingredients. This includes soups, stews, pies, and many other dishes manufactured. Some foods grouped into the previous classes will contain additional ingredients as salted fish or bread, for instance. Yet it is a customary and useful distinction to put into a separate group the foods which contain several major components (in addition to water).

The science of nutrition classifies foods in an entirely different manner, namely, by the major chemical constituents, as proteins, carbohydrates, fats, minerals, and vitamins.

### Food Composition

For many reasons it is important to know the composition of food materials, and the methods for the estimation of many constituents are fairly well developed and standardized (see *Food analysis*). However, foods also contain hundreds of constituents that cannot be estimated easily by present methods. It is now customary to group the major constituents into a few categories to give the "proximate composition" of the food. Tables composed of such data have been prepared for all major raw and processed foods and for important simple and compounded prepared food items (dishes) (4,16,20). Such information must be considered in view of human requirements for various nutrients, many of which have been defined by a number of organizations concerned with food and nutrition.

At the present time human dietary requirements are considered in terms of some forty substances of known chemical composition plus a number of additional factors, the identities of which remain to be established. Malnutrition may result from the ingestion of insufficient food or from insufficient ingestion or utilization of any given required nutritional factor or factors. Thus malnutrition or deficiencies may be caused by lack of certain vitamins or by a deficiency of proteins, minerals, or other factors.

Calorie requirements of man vary widely according to race, age, body size, climate, activity, etc. Such calorie requirements may be satisfied from many types of foods such as carbohydrates and fats, and to a lesser degree, from proteins. Expression of the human body's energy requirements in terms of heat energy is only a convenient measure and an expedient simplification. The requirements of proteins, vitamins, minerals, etc. are also subject to great variations and, therefore, it would seem undesirable to discuss here detailed nutritional requirements. Generalizations are likely to present an incomplete and distorted picture. Charts giving such minimum, optimum, etc. allowances and requirements for various nutrients (calories, fats, proteins, amino acids, vitamins, minerals, trace elements, and water) are now commonly available.

Food-composition tables usually contain values for water (moisture), protein, fat,

TABLE I. Composition of Some Common Foods (in the Edible Portion).

Food	Water %	Food energy, cal./100 grams	Protein, %	Fat, %	Carbo- hydrate, %	Ca, mg. % <sup>a</sup>	P, mg. % <sup>a</sup>	Fe, mg. % <sup>a</sup>	Vitamin A value, I. U.	Thia- mine, mg. % <sup>a</sup>	Ribo- flavin, mg. % <sup>a</sup>	Niacin, mg. % <sup>a</sup>	Ascorbic acid, mg. % <sup>a</sup>
<b>Fruit:</b>													
Apples	84.1	64	0.3	0.4	14.9	6	10	0.3	90	0.04	0.02	0.2	5
Bananas	74.8	99	1.2	0.2	23	3	28	0.6	430	0.09	0.06	0.6	10
Grapes	81.6	74	0.8	0.4	16.7	17	21	0.6	80	0.05	0.03	0.4	4
Oranges	87.2	50	0.9	0.2	11.2	33	23	0.4	190	0.03	0.03	0.2	49
Peaches	86.9	51	0.5	0.1	12.0	8	22	0.6	880	0.02	0.05	0.9	8
Tomatoes	94.1	23	1.0	0.3	4.0	11	27	0.6	1,100	0.06	0.04	0.6	23
Watermelons	92.1	31	0.5	0.2	6.9	7	12	0.2	590	0.05	0.05	0.2	6
<b>Vegetables:</b>													
Asparagus	93.0	26	2.2	0.2	3.9	21	62	0.9	1,000	0.16	0.17	1.2	33
Beans, snap	88.9	42	2.4	0.2	7.7	65	44	1.1	630	0.08	0.10	0.6	19
Broccoli	89.9	37	3.3	0.2	5.5	130	76	1.3	3,500	0.09	0.21	0.9	118
Corn, sweet yellow	73.9	108	3.7	1.2	20.5	9	120	0.5	390	0.14	1.4	12	12
Peas, green	74.3	101	6.7	0.4	17.7	22	122	1.9	680	0.36	0.18	26	26
<b>Miscellaneous:</b>													
Apple pie	—	266	2.9	9.6	42.0	11	22	1.9	0	0.05	0.04	0.4	0
Butter	15.5	733	0.6	81	0.4	16	16	0.2	3,200	Trace	0.01	0.1	0
Bread, rye, light	37.6	263	6.4	3.4	51.7	22	96	0.8	0	0.16	0.04	1.1	0
Ham, fresh	53	340	15.2	31	0	9	164	2.3	0	0.96	0.19	4.1	0
Eggs	74.0	158	12.8	11.5	0.7	54	210	2.7	1,140	0.12	0.34	0.1	0
Cod	82.6	70	16.5	0.4	0	18	189	0.9	—	0.04	0.05	2.3	2

<sup>a</sup> Mg. % = mg. per 100 grams.

crude fiber, carbohydrates, nitrogen-free extract, and less frequently for acidity, vitamins, and ash or mineral constituents (elements of nutritional significance). Water makes up the bulk of all but dried or dehydrated foods.

Two points must always be borne in mind in using food-composition tables for calculations. First, such values are approximations and their meaning is further limited by the use of methods lacking exactness, for instance, by the inclusion of compounds other than fats in the "ether extract." Secondly, such values are averages from which substantial variations will commonly occur. In plant foods, type, variety, climate, seasonal changes, soil conditions, nutritional status of the soil, fertilizers, cultural methods, irrigation, and maturity, as well as many other factors, may cause major variations in chemical composition. In animal products, the number of factors involved are even more numerous but perhaps easier to control. Further variations are then caused by the handling of the harvested plant or slaughtered animal during storage, transportation, etc. Processing will again modify chemical composition, and the variations in compounded foods are indeed limitless. Thus it is remarkable that there is even the limited extent of agreement that is commonly found in the analysis of food products.

Table I shows the proximate composition of some important foods, mostly of plant origin. (See also *Cereals*; *Chocolate and cocoa*; *Dairy products*; *Coffee*; *Eggs*; *Fats and fatty oils*; *Fish and shellfish*; *Meat and meat products*; *Nuts*; *Soybeans*; *Tea*; etc.)

### Food Quality and Its Determination

Besides cost (economy) and nutritional value, quality is the third major factor determining the commercial value of a food. In fresh foods, quality is the sum of factors indicating the extent of success attained in their production. In processed foods, quality will indicate the degree of success with which the desirable properties of the raw material were retained and the typical characteristics of the processed product imparted. The major quality factors in foods of plant origin are discussed here. For factors determining quality of other foods, see the appropriate articles.

**Appearance and color** depend chiefly on the types of pigments present, on the physical characteristics of the surface, and particle size. Surface coatings like the "bloom" on apples may also be a factor. Of the plant pigments, chlorophylls (*q.v.*), anthocyanins, carotenoids, and flavones are the most important. The chemistry of these pigments is now fairly well known and many of them have been synthesized. Color in plant foods can be determined either in extracts by transmission measurements or directly by reflectance measurements. There are a great many instruments in use for such purposes (see *Color (measurement)*).

**Texture and consistency** vary widely in plant foods. Many methods are used for the measurement of the firmness of fresh plant foods, including the pressure testers used for apples, pears, peaches, etc., and the Tenderometer used for peas and other products. The pressure testers measure the force required to drive a plunger of defined size into the tissue. The Tenderometer measures the resistance exerted by a given amount of the plant material against two sets of intermeshing sets of metal disks. Other physical measurements of many types are used, such as viscosity determinations in tomato products and sag measurements on fruit jellies.

**Flavor** is the most difficult quality factor to measure (5). For its evaluation, it

is usually necessary to resort to *organoleptic testing* (systematic judging of flavor by trained persons, under carefully controlled conditions and usually in a manner to give results that can be treated statistically). The chemical compositions of the flavoring and odoriferous constituents of only a few plant products have been completely determined. In most cases, several factors and chemical constituents make up the composite sensation of flavor (see *Flavors*).

For the evaluation of the quality of any given food product, a specific suitable system of determinations of these various factors has to be developed. Such are now extensively used in the evaluation of raw foods, for process control, and for the quality evaluation of processed foods. Attempts to eliminate as much as possible the personal element in quality evaluations led to the extensive use in food grading of objective chemical or instrumental methods, which, however, are available for only a few of the important characteristics of food materials. A composite expression of several quality factors is used for the definition of the grade of many food products. Official grades are widely used for meat, eggs, dairy products, and fresh and processed fruits and vegetables. (See *Food analysis*.)

### Food Production

The goal of food production is to supply palatable, nutritious, and economical food for human beings. With the major exception of sea foods, food materials are produced by agriculture. Over two-thirds of the world's working people are engaged in some kind of agricultural pursuit. While in ancient times, farming and agricultural production was comparatively simple, present-day farming in technically developed countries is a highly integrated, complicated undertaking involving the services of many kinds of specialists. Soil, climate, water, and skill are the primary factors in successful agricultural production (see *Fertilizers*; *Soil chemistry*). The maintenance of soil fertility and productivity are crucial points in agriculture, especially in intensely cultivated areas. Soil-conservation measures, such as the terracing of the land in some parts of the Orient, have been practiced by some peoples for hundreds of years, but in other countries like the U.S. large-scale soil conservation is of comparatively recent origin. Climatology and meteorology will play important parts in determining the types of crops grown, planting dates, etc., while agronomy aids in establishing a desirable relationship between the land and the crops produced and the use of fertilizers. The sciences of botany and horticulture deal with the plant phase of food production, the selection of suitable varieties, cultural practices, etc., while entomology and plant pathology will provide protection of the crops against insects, microorganisms, virus diseases, and other detrimental factors (see *Fungicides*; *Insecticides*). Similarly in animal production, animal husbandry, nutrition, and veterinary science are involved. Agricultural chemistry deals with the chemical and biochemical relationships of all the above sciences involved in the production of food and other agricultural products. One important phase of modern agriculture is genetics, the science of heredity and of breeding new species of plants and animals. Although varieties of cultivated plants were already known in antiquity, great emphasis is placed in modern agriculture on the production of species and varieties which under a specific set of conditions and for a given purpose will produce best results. The breeding of better farm animals and crops of all sorts by selection resulted in substantial improvements in many food products. The spectacular success of hybrid sweet corn might be used as an example of purposeful hybridization.

The bulk of the food produced all over the world is consumed in the fresh form. However, technological developments and refinements in food processing, preservation, and compounding created great industries engaged in food manufacture, using almost exclusively the products of farms. In technologically developed countries, the food industries and the availability of processed foods are important factors from both the standpoints of national productivity and public health. In a nation like the U.S. where some 40% of all people work, the importance of processed foods is obvious. Certainly no adequate diet and nutrition could be provided under such conditions by using the old wasteful and time-consuming methods of marketing and food preparation.

During the past century many specialized food industries became established and some of these reached tremendous volume and value of production. As an example, the sugar industries might be cited. From a negligible production early in the 19th century, the production of cane and beet sugar soared to a volume of 37,000,000 short tons in 1948.

### Food Processing

Most foods in their natural state will stay sound and edible for a comparatively short time only. The fact that grains will keep well on account of their low water content was fully appreciated by primitive man. With the development of pastoral agriculture, milk was preserved in the form of cheese and butter; and by Biblical times, fruit juices were fermented, and peas and lentils, as well as some fruits like figs, dates, grapes, and olives were dried for later use. Fish drying became common practice in Europe hundreds of years ago, and North American Indians dried the meat of buffalo, deer, moose, and bear.

By and large, food-processing developments were slow until about 1800. Smoking, curing, salting, and drying were generally used, but this was the extent of food preservation. Appert, in 1810, published his work on the heat preservation of food materials, and, in the same year, a British patent was granted to Peter Durand for preserving foods by sealing them into a tin-plate canister. During the decades that followed, the canning industry slowly developed simultaneously in several countries. The Civil War gave a forceful impetus to the canning industry in the U.S. There are now over 300 food products preserved in tin cans and hundreds of others in hermetically sealed glass containers.

Cool storage has been practiced for many centuries, but ice did not become much used until about 1800. Late in the 19th century, mechanical refrigeration became available, and this resulted in the rapid evolution of cold storage and ice-cream manufacture, and later of the food-freezing industries.

Food processing is a cooperative undertaking among the agriculturist, the physiologist, the engineer, the bacteriologist, the chemist, and last, but not least, the economist.

The purpose of food processing is to preserve otherwise perishable food materials, to prepare some foods for use, and to produce compound foods of various kinds. The subject of food processing might be discussed either on the basis of the methods used in the preparation of certain foods or according to the principle involved in the processing or preservation.

Chemical engineers look upon food as a fine chemical and accordingly considerable emphasis has been put in recent years on "unit operations" (physical steps like con-

veying, weighing, separation, and mixing) and "unit processes" (steps involving chemical changes, for example, fermentation or hydrolysis of starch and sugars) (2). Unit operations and processes are perceived as a single step in the production, incapable of subdivision, with emphasis on equipment, and carried out in a manner to be economically profitable. Some of the more important unit operations in the food industries may be listed as follows:

(1) Materials handling: conveying, elevating, pumping, trucking and shipping (transportation), etc.

(2) Separating: centrifuging, draining, evacuating, filtering, percolating, pitting, pressing, skinning, sorting, trimming, etc. The processes of drying as well as of cleaning by screening, sifting, and washing fall within this category.

(3) Heat exchanging: (a) chilling, freezing, refrigerating, etc.; (b) heating, cooking, boiling, roasting, baking, frying, etc.

(4) Mixing: agitating, beating, blending, diffusing, dispersing, emulsifying, homogenizing, kneading, stirring, whipping, working, etc.

(5) Disintegrating: breaking, chipping, chopping, crushing, cutting, grinding, milling, macerating, pulverizing, refining (as by conching, rolling, etc.), shredding, slicing, spraying, etc.

(6) Forming: casting, extruding, flaking, molding, pelleting, rolling, shaping, stamping or die casting, etc.

(7) Coating: dipping, enrobing, glazing, icing, panning, etc.

(8) Decorating: embossing, imprinting, sanding, sugaring, topping, etc.

(9) Controlling: controlling air humidity, temperature, pressure, velocity; inspecting, measuring, tempering, weighing, etc.

(10) Packaging: capping, closing, filling, labeling, packing, wrapping.

(11) Storing: piling, stacking, warehousing.

Unit processes used in food manufacture do not easily lend themselves to classification.

Originally, all food-manufacturing processes were batch operations. With the introduction of efficient systems of conveying and pumping and of filling and packaging machines, most processing operations became semicontinuous and in part automatic. At the present time, one of the most important and forceful trends in the food industries is the effort to manufacture foods in a completely continuous and automatic manner. Such processes are, of course, not applicable to all products, but, wherever automatic and continuous production methods have been introduced, at least two major benefits were derived, in addition to the assurance of a more sanitary product. First of all, automatic and continuous lines of production reduce the extent of manual handling and thus the personnel required. This is of especially great importance in food plants open only for seasonal operations. Secondly, automatic equipment lends itself to exact process control and the maintenance of production standards.

Timing is a major factor in food processing and in the harvesting and delivery at the factory of crops and other raw materials produced, in order to utilize full productive capacity and yet not to cause an oversupply. Because the bulk of plant materials used in the food-processing industries are perishable, the difficulties faced, when factors like temperature, sunshine, and rain must be taken into advance consideration, are obvious. Great progress has been made in producing varieties and species of plants with varied requirements in such respects. Efforts to express crop requirements in terms of

temperature-hours or sunshine-hours is one of the important advances in such lines. The difficulties of exact timing are a major consideration in the production of certain types of processed fresh vegetables, for example, corn and peas, where the crop is in its prime for the period of a day or, under certain conditions, for a few hours only. Some vegetables are now snow-iced immediately after harvest. On the whole, fruits can be stored for much longer periods without loss of quality.

The need for speed in processing fresh foods is not restricted to those of plant origin. Animal products will also show quick deterioration and spoilage at times, but here better means are available for controlling or retarding such changes. As examples, the now widely used immediate icing of freshly caught fish and the cooling of animal carcasses may be mentioned.

From the standpoint of design, the requirements of a food-processing plant are similar to those of any other manufacturing establishment. Special emphasis must be put on the abundance and quality of the water supply and on the possible steps that may have to be taken to improve the water available. The water used in food plants must be suitable from the bacteriological (public health) standpoint. When food plants have their own water supply, this is usually purified and chlorinated. Chlorination is also commonly practiced with any water which is re-used in the plant, since this will reduce the chances of re-infection. Of course, a major consideration for water used in food plants is freedom from undesirable flavors and odors of any kind since they would likely be imparted to the foods produced. Alkaline water and high mineral contents are usually objectionable. The presence of undue proportions of calcium and magnesium might cause detrimental hardening of many plant tissues (peas and beans), while metallic ions (iron, copper, etc.) are objectionable for many reasons. The boiler water should be soft in order to avoid excessive scale formation. See *Water, industrial*. Similar requirements hold for ice in direct contact with food materials.

A further major requirement is plant sanitation. Food plants are not only subject to specific regulations and inspections in this respect, but it is now generally recognized that the success in maintaining cleanliness and sanitation often has a direct bearing on the quality and thus on the commercial value of the product. The dairy and infant-foods industries were leaders in this field. Adequate and suitable lighting has now become a part of proper quality control and plant sanitation.

A further difference between a food plant and many other manufacturing plants is the extreme susceptibility of food waste materials to putrefaction and the high biological oxygen demand of waste water. In many instances, considerations of the problems involved in waste disposal lead to the establishment of profitable by-product industries based on formerly discarded materials. The tendency is to utilize every part of the raw materials. This goal has been accomplished to a large extent in the processing of cereals and of meat and other animal products, but not in many branches of the food industries as in vegetable and fruit processing, for instance.

In the food industries (with the possible exception of the cereal products and dairy manufacture) the variations that may occur in the methods of manufacture of the same product are legion (6,12,15,18). Hence only a general description of the major food-manufacturing processes can be given; the preliminary steps in preparing fruits and vegetables for dehydration, canning, and freezing are essentially similar. See also *Alcoholic beverages, distilled*; *Bakery processes and products*; *Beer and brewing*; *Carbonated beverages*; *Cereals*; *Chocolate and cocoa*; *Coffee*; *Confectionery*; *Dairy products*; *Dextrose and starch sirups*; *Eggs*; *Fats and fatty oils*; *Fish and shellfish*; *Flavors and*



*spices; Ice cream and frozen desserts; Malt and malting; Margarine; Meat and meat products; Molasses; Nuts; Pectic substances; Salad dressings; Shortenings; Soybeans; Starch and modified starches; Sugar manufacture; Sweetening agents; Tea; Vinegar; Wines.*

The major reasons that most fresh foods cannot be stored without deterioration and spoilage are the presence of enzymes indigenous to all animal and plant tissues and invasion by microorganisms. Detrimental changes due to other causes such as air oxidation of chemical components occur in some foods but are also often prevented or retarded by proper processing. The methods of food processing and preservation can be classified according to the means applied to control the above factors.

### DEHYDRATION

In dehydration (drying) the water content of a food is reduced to such an extent that enzymes are unable to act and microorganisms are unable to grow. In addition, deleterious changes due to other factors are also usually retarded by a low moisture content. The amount of permissible residual water will vary from product to product according to specific requirements and the length of storage and temperature range to which the product will be exposed between manufacture and consumption. In general, the moisture content of dehydrated food products is in the range of 1–20% (14). At times, products dried by entirely artificial means are called “dehydrated,” in contrast to “dried” products from which the water is removed by sun drying, etc. However, such distinction is largely arbitrary because in actual practice a combination of natural and artificial means is often used, and, furthermore, the commonly used names of many products are contrary to this definition.

The dehydration industry has never become as important in the United States as it has in Continental Europe. During various periods, such as the Civil War and World Wars I and II, considerable efforts were made to increase and improve production, but such efforts were to a great extent abandoned when normal supplies and shipping facilities became available again. The progress made in both dehydration research and production methods during World War II was impressive. The chief importance of dehydrated materials under war conditions is the great reduction in their weight and volume, and the saving in tin required for shipping containers. For 1944–45, the U.S. Army Quartermaster Corps had a dehydrated-vegetable requirement of 157,500,000 lb. (dry) (7). The total production of dried and dehydrated foods in the U.S. in 1948 was 4,414,400,000 lb., of which about 47% was dried bean and peas, about 25% dried and dehydrated fruits and vegetables, and the rest mostly dried milk and eggs (23).

In addition to providing fruit and vegetable products out of season, dehydration has been extensively used in order to compensate for the variations in the seasonal production of some commodities, as milk and eggs. Normally, eggs (*q.v.*) are dried when they can be purchased in large quantities at low prices, but under special conditions, as during World War II, dried eggs were produced the year round.

Quality (including ease of rehydration), cost, and storage behavior are the major factors determining the usefulness of dehydrated products and, therefore, the choice of the method of production used for a given product will depend mainly on these considerations. In order to improve storage behavior, lower moisture levels than have previously been thought commercially feasible are now used, together with replacement of air by inert gases in the hermetically sealed containers into which the dried product

is packed. Storage temperatures are of major importance in maintaining quality and, therefore, as low temperatures as are practicable are used, especially where prolonged storage is required.

**Sun Drying.** Some fruits, like peaches, apricots, figs, currants, and various raisin grapes, are still sun-dried on a very large scale. However, even with these products there is a definite tendency toward the use of the more controllable artificial means.

In order to prevent excessive darkening of the tissues and to improve storage properties, many fruits, such as apples, apricots, peaches, and pears, are sulfured before drying. For this purpose, the fruit is usually placed on trays and placed in a tightly closed sulfuring house where the required amount of sulfur is then burned in metal pans. The sulfuring takes from 15 minutes to several hours. The amount of sulfur taken up by the fruit will be greatly influenced by the temperature as well as the sulfur dioxide concentration. The desirable extent of sulfuring will depend on the product but is generally in the range of 1000-3000 p.p.m. sulfur dioxide. Most of this sulfur dioxide is lost during drying.

Some fruits like figs must be fumigated before drying in order to prevent infestation by various insects. Usually, either chloropicrin, ethylene oxide, or methyl bromide is used. In order to hasten the drying, some fruits, like certain types of raisins, are dipped into a dilute solution of alkali upon which a film of edible oil is floating. Such dips may be applied cold or hot.

Sun drying requires several days and is followed by "curing" in sweating bins where the moisture in the various pieces equalizes. The dried fruit is then graded, at times resulfured, and packaged. The water content of most dried fruits is in the range of 5-20%, with different requirements for various fruits.

**Artificial Drying.** The basis of successful drying is the transfer of water vapor into a stream of air or other gases that are not saturated with water vapor. Therefore, the volume, temperature, and the relative humidity of the drying gas and the surface of moist material exposed to it will govern the drying efficiency. The design of drying equipment is a specialized branch of engineering and, in the planning, the nature of the material to be dried will be of major consideration (see also *Drying*). Every food particle has a definite attraction for moisture, which at a given temperature and pressure will be in equilibrium with the moisture content of the drying atmosphere. This attraction to moisture as well as the size (surface) of the particles to be dried vary greatly, and, therefore, most types of dehydrating equipment will be suitable for a limited number of products only. With foods, the effects of the drying on flavor, color, physical condition, and nutritional value are further factors that must be taken into consideration.

For fruits and vegetables, cabinet, kiln, tunnel, and various sorts of vacuum dryers might be used. Sulfuring is often desirable.

A *cabinet dryer* consists of a drying chamber usually divided into several compartments, each holding one or several stacks of trays mounted on trucks. The cabinet is usually heated by steam coils, through which an air movement of 600-1200 linear feet or more per minute is maintained. Circulation is usually across the trays.

The old-fashioned *kiln dryer* or "*evaporator*" is a two-story structure. The product to be dried (mostly apples and apple pomace) is placed in the upper room, which has a slatted floor. Underneath, a stove or furnace heats the air, which, by means of pipes, vents, or fans, is distributed to provide fairly uniform heating at various points of the drying chamber. This dryer is rather inefficient but inexpensive to construct.

*Tunnel dryers* are used extensively and were found efficient and practical during the recent years of large-scale production. Here the drying takes place in tunnels 30–50 ft. long and about 6 ft. square. The material to be dried is loaded upon slatted wooden or metal trays stacked on trucks, which fit the tunnel snugly so that the air passes between and across the trays. The loaded trucks are introduced through the door at one end of the tunnel, and the dried material is removed at the other end. Air movement in the tunnel might parallel the direction of movement of the trucks, or be countercurrent, or might combine parallel flow at the entrance half and countercurrent flow from the center to the dry end where the dry product is removed.

In some tunnel dehydrators, the material to be dried is moved on a belt in a tunnel-like chamber; while in others, the whole process will take place in a cabinet within which a stainless-steel belt moves the material at different levels and in various ways.

A variety of heating systems are used for tunnel dryers, and usually the air flow is regulated to give a velocity in the range of 150–1000 linear ft. per minute, according to the requirements of the product and to the extent to which the hot air is forced through the material. For the sake of economy, a part of the air is recirculated in most tunnel dryers.

*Vacuum shelf dryers* provide more rapid drying at lower temperatures but they require expensive equipment and are now used to a limited extent. A specific form of vacuum drying is drying from the frozen state or freeze drying (8) (lyophilization), which was highly developed during World War II for producing materials other than foods (see Vol. 5, p. 258). The product is dried by sublimation of the water without raising the product temperature, a point of utmost importance from the flavor standpoint. Freeze-dried foods also possess advantages in rehydration. Because of its present high cost, freeze drying is used for specialties only. Continuous vacuum dryers also have been used to a very limited extent. While the present importance of vacuum equipment is limited in the total scheme of food production, it is regarded by many as a field of food processing pregnant with important practical developments.

*Drum dryers* have been used for many years for milk, fruit juices, pulped fruit, and meat, as well as soup mixtures and other foods. Drum dryers are 2–6 ft. in diameter, either single or double, and are heated from the inside, and the outside surface is used for drying. In the common type of double-drum dryers, the material to be dried is placed between the rolls into the top “well,” where the rotating drums pick it up. The drying is then completed by the time the material on the drum reaches the scraper or “doctor blade,” which shaves off the dried product. The material to be dried may also be fed from a shallow pan under the drum or sprayed on the drum (see *Dairy products*).

In vacuum drum dryers, the whole operation is conducted in the same manner in a vacuum, providing means of more rapid drying at lower temperatures. Drum dryers kept in an inert atmosphere have also been used.

*Rotary dryers* are long, revolving, metal cylinders provided with devices to keep the material in it moving in the inside. They are heated by steam coils or preferably by hot air, or combustion gases. As with tunnel dryers, the air stream may be concurrent or countercurrent. They are used mainly for meats, apple pomace, citrus pectin pulp, and more extensively in the drying of alfalfa and (limed) citrus peel, etc. for animal feed. They may be portable, for drying hay “in the field.”

*Spray dryers* are used for milk, whole eggs, egg yolks, fruit and vegetable juices and purées, soluble coffee and tea, and several other food products (19). In this

method, the material is finely atomized, usually at the top of and into a large cone-shaped chamber in which heated air is circulated. The droplets carrying the solids are dried during their passage through the heated air or gas, and the solid particles are trapped by a collector, which usually consists of a second smaller cone-shaped structure. There are many different designs of spray dryers based on various principles and constructed for specific purposes. It is the quickest means of drying but applicable to a limited number of foods only. The installation costs are high (see *Dairy products*).

Often it is most expedient to use combinations of various procedures for dehydration. There are some vegetables that can be most economically dehydrated with a maximum retention of desirable properties by first using a tunnel dryer to remove the bulk of the water, followed by drying in cabinet dryers, and lastly by removing some more moisture in bins through which air dried by silica gel is circulated. Some dehydrated-food products are now manufactured with residual moisture contents under 1%. As an example, an outline of the procedure for producing dehydrated cabbage shreds by cabinet or tunnel dryers is as follows (3):

*Fresh or stored cabbage*—of suitable variety, maturity, and condition.

*Washing*—mostly to remove soil, etc.

*Trimming*—outer leaves removed by hand.

*Coring and shredding*—by machines used in sauerkraut manufacture; shreds usually  $\frac{3}{16}$ – $\frac{1}{4}$  inches in width.

*Sulfuring*—by dipping for 20–30 seconds into a 0.10–0.25% sodium sulfite solution at 200°F.

*Blanching*—in flowing steam for 2–3 minutes, or sufficiently to inactivate catalase in the tissue.

*Traying*—1 lb. or less of shreds per square foot of drying surface.

*Dehydrating*—starting air temperature can be high since evaporation of water will reduce cabbage-shred temperature; finishing temperature should not exceed 145°F.; time required 4–6 hours.

*Finishing*—in bin with an air flow at 110–130°F. for 3–5 hours; final product contains below 4% moisture and not less than 750 and not more than 1500 p.p.m. of sulfur dioxide.

*Inspecting and packaging*—usually into square, hermetically sealed, metal cans made of tin plate.

Potato flour (or powder) is produced either by grinding and bolting dehydrated shredded or riced potatoes, or by drum- or spray-drying a slurry of cooked potatoes. Potato flour is extensively used in soups in the U.S. and in baking in Europe.

#### CANNING (THERMAL PROCESSING)

Fresh foods almost invariably carry or will eventually acquire microorganisms that cause spoilage. The principle of preservation of foods in hermetically sealed containers rests on the destruction by heat of such organisms in a closed container, which prevents reinfection. Suitable containers may be made of metal, glass, or many other materials. This method of preservation is called canning (or, better, thermal or heat processing). It is clear that in addition to the destruction of microorganisms, the enzymes present in the food will also be entirely or mostly inactivated.

The canning industry in the U.S. is one of the largest branches of the food industries. In 1948, the total production of canned foods in the U.S. was about 567,000,000 cases, of which fruits and vegetables accounted for 211,600,000 and juices for 114,800,000 cases (23). The rest of the production was made up of baby foods (16,900,000), meats (23,600,000), milk (81,100,000), nonseasonal vegetables (53,100,000), poultry (2,100,000), soups (42,000,000), and fish (21,800,000). The total amount of foods processed in glass containers (which comes under the definition given above for canning) consisted of 217,000,000 cases in 1948, of which 30,000,000 cases represented fruit preserves like jams, jellies, fruit butters, marmalades, etc. The total value of

processed fruits and vegetables in 1948 was \$395,900,000 and of fisheries products \$34,122,766. See also *Fish*.

Large canning industries exist in all technically developed countries, and a considerable proportion of the international trade in foods is in canned products.

While properly prepared canned foods will keep indefinitely as far as putrefaction is concerned, deterioration of quality and of nutritive value will occur during the prolonged storage of many products. This point was well illustrated during World War II by the spoilage of many canned foods stored under tropical conditions and led to extensive investigations of storage behavior. It is now well appreciated that when extensive storage is necessary, canned fruits and vegetables should be kept at temperatures below 50°F. Freezing does not usually affect the quality of most canned products although occasional slight deterioration in the texture has been noted, especially upon repeated freezing and thawing (1).

The term "processing," as used in the canning industries, means the cooking of the product in the sealed container (of metal, glass, or other materials); it is designated in terms of temperature and time of the thermal treatment required. The processing of a canned product must destroy all organisms that are injurious to health and that might cause spoilage. Complete bacteriological sterility, while sometimes attained, is not always essential in canned products, providing that conditions in the can are such that no growth of such residual organisms will occur.

*Blanching* is almost universally used with canned vegetables. The purpose of such treatment, usually performed by steam or more commonly by immersion into hot (160–210°F.) water, is to remove from the product adhering materials (especially dried plant juices), which might injure flavor during storage of the product, and to drive out air and other gases from the plant tissue and to wilt or swell the tissues to allow a better control of the filling operation. In certain cases, blanching improves the color of the product and in others it functions as a means of destroying the enzymes present in the tissues. This latter is often desirable in spite of the almost universal inactivation of enzymes during subsequent processing.

Extensive studies of blanching and its effect on the quality and nutritional value of various products led to the tendency to shorten heating periods and elevate blanching temperatures. In the case of peas, for instance, the use of times exceeding 5 minutes and of temperatures below 180°F. is now mostly obsolete. The preferred blanching time has been shortened and the water temperature raised to 190°F. or higher. In blanching, as in any other heat treatment, the heating of the center of the product will determine the required time, and thus longer times will be applied in case of larger pieces, as larger-sized peas, for instance. This inequality in the required blanching time is one of the reasons for sorting vegetables like peas and green or wax beans according to their sizes.

Blanching equipment of a great variety is now in use. The tendency is to have completely automatic temperature control together with recording instruments charting process details which are available later in case any abnormalities are observed in the product. It should be noted that most vegetables are also blanched before dehydration or freezing.

The reasons for the preheating of tomatoes used in the manufacture of macerated products like juice, purée, paste, and catsup, are somewhat different from those for the blanching of vegetables. In tomatoes, enzyme systems naturally present tend to

destroy some useful constituents (pectins) of the tomato fruit, and rapid heating to temperatures above 180°F. will be needed to eliminate such detrimental effects, especially in products where consistency is of major importance (17). It has also been claimed that the preheating of tomatoes will increase the yield of juice, but this still is a moot question.

*Filling* of the cans is now almost universally accomplished by the use of machines. However, there are some products like sardines, asparagus, and a few others for which machine filling is impractical; so these are filled by hand. In many cases, as with whole tomatoes, the filling is semiautomatic through the use of equipment that aids in hand filling. The modern filling machine is one of the impressive accomplishments of technology. Such machines are often capable of filling over 500 cans or glass jars per minute. Obvious variations in the desired speed of filling will result from the nature of the product, from the method of filling used, from the size of the can used, etc.

Immediately after filling, the cans or jars are often "brined" or "siruped," by adding a hot dilute solution containing sugar or salt or both. At times, water is used to fill the cans after placing the required weight of material in the can. In the case of tomatoes, the cans already containing the tomatoes are filled with tomato juice.

*Exhausting* is often practiced in order to preheat products such as whole tomatoes, peaches, and apricots that cannot be filled hot or sufficiently hot in order to remove gas or air from the can's contents before closing the can. Exhausting is also important in order to obtain satisfactory vacuum in the product (see below). The customary way of exhausting is to pass the filled cans through a steam chamber or hot-water bath of the required length.

*Sealing* of the cans is now universally accomplished by automatic closing (seaming) machinery, often of high capacities, approaching the speed of filling. The empty cans are received by the processing plant in paper-lined box cars or trucks together with the covers in separate containers. However, there are a few products, for example, evaporated or condensed milk, which are filled into the completely preformed can through a hole, which is then closed by solder dipping or seaming, depending on the position of the hole.

Sealing compounds of various sorts are used to provide a hermetic closure between the can body and the top, and then the closing machine double-seams the can by curling up the edge of the cover with the flange of the can. After curling, the seam is flattened, and, with the sealing compound in the seam, a hermetically sealed container is obtained. Such a simple description hardly does justice to the intricate and ingenious operations involved in this process. In glass jars, the increasing tendency is to use covers which are held on the container by the vacuum.

It is generally desirable to have a partial vacuum in the hermetically sealed container after the product is finished. This vacuum may be obtained by a number of different means. If the product packed into the can or jar is well heated by the time of closing, a partial vacuum will result on cooling. This is one reason for packing the products hot, using hot brine, and exhausting. Mechanical means are also often used to obtain a vacuum and in such cases the can is sealed in a vacuum chamber. Another method of increasing the vacuum in the can is the "steam-flow-closure procedure" in which a jet injects the steam into the head space to replace the air as the cover is placed and then sealed on the can.

The vacuum in the can has several important functions. It will reduce the strain on the can and prevent buckling ends. This is especially important in canned prod-

ucts exposed to high altitudes or tropical temperatures. The vacuum will also aid in most cases in better retention of the quality and nutritional value of the canned product. Finally, in the case of many acid products, the reduction of the partial pressure of oxygen will result in improved resistance of the tin plate to corrosion. Too high vacuum in large cans will result in paneling or drawing in the side of the can. The vacuum produced in most canned foods is in the range of 7-15 in. of mercury. It should be noted that the term "vacuum-packed" does not refer to the presence of vacuum in canned foods (now almost universal), but to the fact that the product has been packed without or with a minimum amount of brine or sirup, and the can closed on a vacuum sealing machine. Such products, just like others, will require subsequent thermal processing.

*Processing times* will depend on several factors. Of these, the nature of the can's contents, especially its pH and physical state and the size of the container, will be the governing factors. A further important consideration will be the air space in the can (fill of container) and the type and number of various microorganisms that remain in the product after preparation and at the time the can is sealed. In the early days of the industry, minimum processing times were determined in an entirely empirical manner, but now sufficient scientific information is on hand to allow extensive computations of such values.

The penetration of the heat into the can is one of the important factors in the calculation of processing times. Liquids are heated mainly by convection while solids are heated only by conduction, but all intermediates between these extreme types of heat penetration will occur in some of the great variety of products which are heat-processed. In general, the more nearly liquid is the product, the better will be the progress of heat into the can's contents. Rotating or rolling cans containing liquid products will further enhance the progress of heat penetration. Since the governing factor will be the time needed to reach the required temperature in the center ("cold-spot") of the can, the effect of can sizes is obvious. The progress of heat penetration is often determined by using cans or jars containing a product artificially infected by a given number of a known organism followed by determinations of the survival of such organisms or by sealing into the container thermocouples through which the progress of the heating in different parts of the can can be measured.

A further important factor in processing is the pH of the product, since the resistance of microorganisms to heat will depend on this factor. Acid products, such as fruits, fruit juices, and preserves, need much less processing for sterilization than do more neutral vegetables, like beans and peas, as well as meat products. Since thermal processing of neutral products at atmospheric pressures will require long periods, which are objectionable from both the standpoints of the product's quality and production efficiency, higher processing temperatures must be used. At first, salt and calcium chloride brines were used to raise the boiling point of the sterilizing (processing) baths, but, now, processing under pressure is universally practiced. Automatic, continuous, pressure cookers are now used for many products and the use of such equipment is on the increase.

Because of these many variants, a wide range of processing times is used in the canning industries. Any processing procedures will also depend on the type and size of the container and, since factors like the residual infestation by microorganisms, consistency, etc., will differ at times, constant vigilance and adjustments are required on the part of canning technologists.

*Cooling* of all canned products after processing is the last important operation in commercial processing. Since lethal temperatures will persist in the cans at the moment when they leave the retort or bath, the type and extent of cooling are important and usually regarded as part of the process. Cooling is necessary to avoid undue softening of many products as well as possible objectionable changes in color and flavor. *Air cooling* is used in cases where either prolongation of heating is desirable or where heat does not injure the quality of the product. The rate of cooling here is slow and depends on the air temperature and movement, as well as on the pattern in which the finished cans are stacked. *Water cooling* is much more common since in most cases additional heating beyond the exact processing time is regarded as detrimental to quality and nutritional value. The hot cans may be cooled by admitting water into the retort in which they were processed or they may be cooled after removal from the retort by immersion in cold water, usually by conveying the cans mechanically through water tanks or showers. *Pressure cooling* is often used with large or irregularly shaped cans and glass containers, where undue strain would be exerted on the containers by releasing the pressure. This is avoided by maintaining pressure on the containers during cooling to counterbalance the pressure produced within the can during the process.

Cans are usually water-cooled to about 100°F., although in certain cases cooling is continued until the product temperature reaches 60–70°F. Most canners prefer to cool to 100°F. because at this temperature the drying of the exterior of the can is still rapid.

*Casing and warehousing* may be undertaken immediately after water-cooling cans and after a proper cooling period with air-cooled containers. A variety of machinery is used to reduce the extent of manual handling formerly required in labeling and placing the cans or other containers into cases. The latter are now usually made of paper-board. In most canning factories dealing with seasonal products, labeling and casing are undertaken after the end of the packing season.

The beneficial effect of comparatively low temperatures in the storage of canned products has been already noted. Many canners employ insulated or even refrigerated warehouses, especially when the canned goods must be stored through the summer months.

As an example of a commercial canning procedure, that used in the canning of green peas is illustrated in the following outline:

*Harvesting of pea vines*—at the time determined by the factory field man.

*Separation of peas*—in the pea viner or podding machine; vines to silage.

*Cleaning, weighing, and boxing*—blast of air is used for cleaning and then the peas are put into lug boxes, shipping cases, etc., and chilled with cold water or chipped ice if transported any distance.

*Maturity determination*—at the factory by Tenderometer; together with yield, this reading will determine value of crop and payment to grower.

*Washing and size grading*—in squirrel cages, etc., and in sizing machines, which will separate peas into a predetermined number of size groups.

*Quality grading*—according to specific gravity by flotation in brine; this may be done after blanching.

*Blanching*—in hot water of 185°F. or above for 5 minutes or less.

*Washing*—by water spray.

*Filling*—by automatic machine into enameled cans to about ½ in. from top.

*Brining*—with hot dilute solution of salt and sugar to within ¼ in. of top.

*Exhausting*—for a short period is used occasionally.

*Closing*—sealing; the can tops are coded during this operation.



*Processing*—25–55 minutes at 240°F., depending on size of can and size of peas.

*Cooling*—to below 100°F.

*Labeling, casing, warehousing, grading, and shipping.*

**Fruit Juices.** Although canned (heat-preserved) fruit juices were prepared from a variety of fruits in many countries for over a century, their large-scale production did not commence until the 1930's (22). In 1929, the total amount of fruit juices packed in the U.S. was only 390,000 cases. By 1935, the total pack was 18,000,000 cases and, in 1940, 45,000,000 cases of various juices was produced. In 1948, the total production was 114,000,000 cases as compared with 4,100,000 cases of vegetable juices (excluding tomato juice) (23). In this latter year, citrus juices and tomato juice made up about 65 and 24%, respectively, of production. Apple juice, one of the first fruit juices packed commercially, is produced in considerable quantity in Europe, but in the U.S. it has a comparatively subordinate position, representing now only about 1% of the fruit-juice pack.

While these statements refer to heat-preserved fruit juices, to be used as such, very great quantities of citrus juices (especially orange juice) and tomato juice are used to make concentrates of all sorts, including a variety of products like tomato purée, sauces, paste, etc.

While the fruit-juice industry originally utilized mostly surplus fruit and such as were unsuitable for the fresh market or processing, now most fruit juices are produced from fruit specifically produced for such purposes.

*Apple juice* is pressed by hydraulic presses from washed, crushed apples. In some countries like Switzerland, pears are blended with apples to give a more suitable product. Apple juice may be marketed in the cloudy form or clarified by a variety of different means, of which clarification with gelatin and tannin, with bentonite, and by the use of pectolytic enzymes may be mentioned (see *Enzymes*; *Pectic substances*). The preference in the U.S. is about equally divided between clear and cloudy juices. A cloudy juice is favored in France, while in Switzerland, Germany, and Great Britain brilliant apple juice is preferred. A further product which should be noted here, although it does not come within the exact definition of apple juice, is "liquid apples" or "crushed apples," in which the bulk of the apple tissue is included in a finely comminuted form. The product is sterilized either in the final container or preferably before filling in high-speed, high-temperature pasteurizers with a short additional heat treatment in the final container. In Europe, clarified apple juice is often stored in bulk under carbon dioxide pressure and refrigeration and packed aseptically after germproofing filtration. Such methods produce an apple juice void of any objectionable cooked flavor. Large quantities of apple juice are used in the manufacture of (fermented) cider and brandy.

Fresh apple juice is subject to rapid fermentation, and this has led to a certain amount of confusion in the terminology. Cider or fresh cider as used in the U.S. means the freshly pressed or preserved juice of apples, while hard cider or fermented cider is the product resulting from various stages of alcoholic fermentation and containing 0.5–8.0% alcohol. The term apple juice first came into general use with the development of canned (heat-processed) fruit juices. However, in many European countries the unfermented juice is designated apple juice or apple must, and the term cider is reserved for the fermented product (19a).

*Citrus juices* are produced by a variety of means of which reaming of the half fruit is perhaps the most successful. One of the problems in citrus-juice production is the

removal of the juice without getting an excessive proportion of peel oil and albedo (white) constituents into the juice, since these will give it a bitter flavor. A further problem is the retention of the "cloud" or cloudiness, which results from the ability of some natural constituents to hold the minute tissue particles in suspension. This is usually accomplished by the rapid heating to destroy the enzymes acting upon the constituents involved in this emulsification (see *Pectic substances*).

From the "juicers," the juice flows through screening equipment to remove seeds and undesired suspended particles. This is usually followed by de-aeration and filling into cans, which are then quickly sterilized under hot water with rotation to insure rapid heat penetration. Cooling follows the processing. Tubular flash heaters are also often used for citrus juices. Large quantities of concentrated citrus juices are now frozen (see p. 805).

*Grape juice* was the first fruit juice produced on a large scale in the U.S. Mostly the Concord grape and some very similar related varieties are used for this purpose. After washing, the grapes are mechanically stemmed, since stems would impart an undesirable flavor to the product. Then the grapes are heated in steam-jacketed kettles to 135–160°F., and pressed in the rack-and-cloth type of hydraulic presses. The fresh juice as it flows from the presses is naturally supersaturated with potassium acid tartrate, which precipitates out during subsequent storage (*argols*). Some grape juice is produced by straining and centrifuging or by freezing, thawing, and filtering immediately after the juice is pressed. Before bottling, most grape juice is stored in glass carboys or in bulk, usually in concrete or wooden tanks and under refrigeration. For packaging, the juice is siphoned off and at times filtered. Clarification by pectolytic enzymes might be undertaken before siphoning and filtration. Most of the juice is then bottled hot and pasteurized in the bottles by holding these for the required time in a hot-water bath. The argols are universally recovered.

*Tomato juice* production in the U.S. increased from 185,000 cases in 1929 to 27,800,000 cases in 1948, one of the most spectacular developments in food processing (23). Fruit is usually graded as it enters the factory and is then washed and trimmed. The juice may be extracted cold or after heating of the fruit ("cold break" and "hot break"). As already indicated, there are certain advantages derived from preheating the fruit to 180–185°F., either in steam-jacketed kettles or, immediately after chopping, in steam-jacketed heaters in which the tomatoes are moved by a screw device, or in tubular heaters. The tomatoes are then "juiced" or "extracted" by putting them through an instrument consisting of a perforated stainless-steel jacket placed around rotating blades, which will squeeze the juice and soft parts of the fruit through the perforations without beating too much air into the product. The juice is often put through a second such device possessing smaller perforations or through a homogenizer of some sort. The "finished" juice is heated to about 180°F. (unless the juice is already at this temperature) and salted either at this point or by adding salt from a spoon or in form of a tablet to the can after it has been filled. Now the cans are closed, processed for 15–40 minutes (depending on the size of the cans) in boiling water, and cooled. The tendency now is to use high-speed tubular heat exchangers to heat the juice for a fraction of a minute to about 250°F., followed by immediate cooling to the filling temperature of about 185°F., and filling. No subsequent thermal treatment is used in this case.

The concentrated tomato products (purée, paste, etc.) are usually made from juice produced by the hot-break process by concentrating in multiple-effect evapora-

tors. Various blends of tomato juice with other juices (especially from vegetables) are also packed and seem to be gaining in popularity. One reason for this is that by proper blending of such products a constancy of flavor can be attained, while variations in the flavor of tomato juice from different lots of tomatoes and in different seasons will unavoidably occur.

**Home Canning.** No discussion of canning is complete without a mention of home canning. Although its extent is difficult to assess, it is clear that home preservation of perishables by this process is commonly practiced in the U.S. as well as many other countries, especially in Europe. The list of products canned by homemakers is endless and includes fruits, vegetables, meats, chicken, and various fruit and vegetable products like jams, jellies, and relishes. The economic and nutritional importance of home canning lies in the utilization of large quantities of perishable foods in their prime condition. Home canning effects considerable saving in cost and often makes substantial contributions to the family diet. Home canning attains additional importance in periods like the years of World War II, when most commercial canneries in the U.S. were limited in the amount of tin plate available and were already exerting themselves in fulfilling government orders for the armed forces.

Home canning developed together with the canning industry. From strictly empirical and often haphazard methods, the home canning of various products became an operation based on scientific principles. In the U.S., the major credit for this change goes to various government agencies, especially to the U.S. Department of Agriculture, and to the various state colleges and experiment stations, which for many years provided expert assistance and advice in simple words and simple techniques applicable in the home. A major development in this field was the introduction of home pressure cookers now generally used with low-acid foods.

#### COLD STORAGE OF FOODS

When the temperature of storage is lowered, most foods will keep longer. The multiplication and growth of most microorganisms is thereby reduced, and enzyme actions and other processes in living tissues as well as nonenzymic reactions leading to deterioration and spoilage progress more slowly. However, as a rule, cold storage does not stop such changes but merely retards them. As temperatures are again elevated, all three types of reactions will again progress at increased rates. Although cold storage has been used for thousands of years, the intercontinental shipping of food, especially from New Zealand and Australia to England, provided a major impetus for the development of modern cold-storage technology.

Cold storages are extensively used with a wide variety of products and under a great variety of conditions. Fruits, vegetables, dairy products, eggs, meat, meat products, fish, and many other foods are held in cold storage from periods ranging from a few days to a year or more.

Although icing is still extensively used, artificial refrigeration is being increasingly applied. The art of heat removal or refrigeration (*q.v.*) is a highly specialized branch of engineering. In addition to the initial cooling and heat losses, calculations of refrigeration loads and capacities must also take into account the heat generated by living tissues. For instance, 1 ton of sour cherries at 60°F. will evolve 11,000–13,200 B.t.u. per ton per day (15). A number of other factors will also enter into the calculations of refrigeration requirements and thus into the design of refrigeration equipment. A considerable variety of different types of mechanical refrigeration and refrigerants

are now in use. Capacities of refrigerating equipment are usually expressed in terms of ton refrigeration. A ton refrigeration is equivalent to the removal of 288,000 B.t.u. per day or 200 B.t.u. per minute.

For best storage, most products require a specific, often narrow, temperature range, a given humidity, and perhaps also atmosphere control. The variations in all these requirements are great. Atmosphere control is important from the standpoint of odors as well as the presence of gases. Some products emanate gases, which influence the storage behavior of the same product as well as that of other commodities. Artificially introduced gas atmosphere is often used for the storage of foods. Sometimes such desired gases are produced by the food and then kept at specific desirable concentrations.

Most *fruits and vegetables* keep best at 32°F., but the optimum storage temperatures for some products like lemons, grapefruit, cucumbers, tomatoes, and potatoes are somewhat higher. Often the optimum storage temperature (and other conditions) for a given crop (like bananas) will change with the maturity.

*Milk and cream* must be held under refrigeration at all times and are usually kept near 32°F. Even at this temperature these products will keep only for a few days unless they are pasteurized and cooled before being put into cold storage. In pasteurization, the number of microorganisms in the milk is greatly reduced and the pathogenic organisms are killed (see *Dairy products*).

*Fresh meats* are highly perishable and therefore must be cooled immediately after slaughter and kept just above the freezing point until used. Some meats become more tender during aging. Cold and freezing storages of all sorts are extensively used with meats and meat products (see *Meat*).

*Fresh fish* is even more perishable than meats, and the present tendency is to ice or refrigerate fish immediately upon catching. Salted and smoked fish will also keep better at lower temperatures and are often kept under refrigeration (see *Fish*).

*Eggs* are usually kept at 31°F. where, under proper conditions of humidity and control of air movement, they will keep for many months (see *Eggs*).

A great variety of other foods and food products are kept in cool storage. Of these, wines, various chocolate products, yeast, and nut meats may be mentioned. Cold storage is also extensively used during the transit of perishable foods by various means.

#### FREEZING AND FROZEN STORAGE

The development of the food-freezing industries since about 1925 has been spectacular. Although small quantities of food, especially fish and eggs, were frozen before, the large-scale freezing of fruits and vegetables and meat commenced during the 1930's. By 1945, the amount of fruits, vegetables, fish, fowl, and eggs frozen in the U.S. reached 1,466,000,000 lb., of which 739,000,000 lb. was fruits and vegetables. In 1948, the U.S. frozen-fruit and -vegetable pack was 824,000,000 lb. with a value of \$170,000,000. The remarkable speed with which some industries have developed and the products have been accepted by the public is indicated by frozen citrus-juice concentrates, of which only about 2,500,000 lb. was produced in 1946, increasing to 6,000,000 lb. in 1947, 27,500,000 lb. in 1948, and 136,700,000 lb. in 1949, with further increases in production since.

The amount of fruits and vegetables frozen in the United Kingdom increased from 4,400 tons in 1947 to 6,400 tons in 1948 (1a). The increase in frozen fish was even

more spectacular: from 9,394 tons in 1947 to 20,036 tons in 1948 (9). Quick-frozen fish-and-chips are now produced in Scotland. In Australia, the fruit- and vegetable-freezing industry is still in its infancy, but rabbit carcasses and prawns have been frozen on a large scale for some time.

The earlier developments of the dairy and ice-cream industries in the U.S. have paved the way for the evolution of the freezing industries. The widespread processing, storage, distribution, and use of frozen foods would not be possible without the extensive network of freezing storages throughout the country. In addition to the warehouses kept at suitable freezing temperatures, the availability of mechanically refrigerated rooms and cabinets throughout the distribution system and the use of deep-freeze cabinets, lockers, and refrigerators by the ultimate consumer were of utmost importance.

A further factor in the development of the frozen-food industries in the U.S. and in Europe was the increasing general appreciation of quality products and, in the U.S., the premium put upon convenience. This latter point is well illustrated by the extensive manufacture of frozen half-finished and finished items (dishes) and of whole meals. Last but not least, the high purchasing power, which allowed some disregard of economy in favor of quality and convenience, certainly contributed to the rapid evolution of this branch of the food industries in the U.S.

Whereas cold storage will only retard the three major types of detrimental changes in foods, those of microbial, enzymic, and nonenzymic origin, freezing will often completely arrest these changes, and in some cases slow them down to such an extent as to allow storage of the product (11,21). However, in order to assure better storage behavior of plant foods, it is often desirable to inactivate some of the enzymes present in the tissues. It is clear now that such thermal inactivation of the enzymes (blanching) will usually destroy only certain enzymes while others will survive. The roles played by different enzymes in the deterioration of frozen foods is not clearly understood at the present time.

In many cases, the freezing of a food, as meat, will cause no objectionable physical changes or will be even beneficial in certain respects. In other instances, the alterations resulting from freezing and thawing will be objectionable. Most such changes seem to be caused by the formation of ice crystals in the tissue and by the irreversible disturbance of colloidal tissue components. Quicker freezing will result in the formation of smaller ice crystals and thus in less disturbance of tissue organization. As far as flavor, odor, and color are concerned, the changes caused by freezing are usually less marked than when the same foods are canned. On the other hand, there are many products which, by their very nature, must be prepared by a given method. Tomato juice, for instance, usually lacks the typical flavor associated with this product if it is prepared without heat treatment and then frozen, rather than processed by heat in the usual manner.

Siruping or mixing with sugar is used with many fruits in order to assure better quality in the frozen product. This is the case with apples, strawberries, raspberries, peaches, apricots, and cherries, which make up the bulk of frozen-fruit pack. In order to prevent oxidative discoloration of sliced peaches, addition of ascorbic acid (*q.v.*) to the sirup is now common practice. Most vegetables are blanched before freezing; sulfuring is used only with fruits and to a very limited extent.

The rate of freezing will depend on the efficiency with which heat is removed from the product to be frozen. The first phase of the freezing process consists of chilling

the product to its freezing point. During the second phase, the actual freezing, the temperature of the commodity remains practically constant. The third phase is the lowering of the temperature of the frozen product to that required for its storage, which is usually considerably below the freezing point. The first phase is usually easily accomplished because of the relatively large temperature difference between the warm food and the refrigerating medium. The amount of heat (plus latent heat of fusion) that will have to be removed during the freezing process will vary from as low as 22 B.t.u./lb. for dried beef to 124 B.t.u./lb. for milk and 144 B.t.u./lb. for water. Fruits and vegetables are in the range of 100-134 and fresh meats in the range of 66-100 B.t.u./lb. Thus the rate of freezing of different products will vary considerably when the same equipment is used for various foods. Although for some time it was believed that quick freezing generally results in products of higher quality, it is now clear that this is seldom the case. However, under certain conditions, rapid methods of freezing have advantages over slow freezing. First, quality deterioration might occur in a product during the first phase of the freezing process during which the temperature of the product is reduced to its freezing point. The possibility of such deterioration is reduced by quick freezing. Second, the output per unit investment is usually higher in equipment capable of quick freezing.

There are three main **direct-contact freezing methods**, with many variations.

*Freezing in still air* was the method commonly used for a long time. The product is placed into a refrigerated room, well insulated, and usually kept at 0°F. Freezing under such conditions is slow and uneven: for a barrel of berries it might take 10 days and even small packages will require 6-10 hours for complete freezing.

*Blast freezing* involves the use of powerful blowers that circulate the air in the freezing room. The high velocity of the air makes it an extremely good medium for heat transfer. At times, blast freezers are constructed in the shape of tunnels into which the product is introduced on trucks loaded with the food to be frozen. A further modification of this process is the use of a tunnel in which the product is moved on endless wire-mesh belts. This method was originally designed for use with cut corn but is at times used for other products.

*Immersion freezing* was originally used for freezing fish by direct immersion into a mixture of ice and salt or brine. This method also has been used with packaged products, although the objection has been raised that the submersion into the freezing brine will enhance the corrosion of tin cans. A modification of this method is one in which the freezing brine is sprayed on the product. Sugar sirup is used instead of brine for the immersion freezing of products (berries) where the traces of salt picked up by the food are objectionable.

In **indirect-contact freezing**, the freezing is accomplished by the freezing medium (usually calcium chloride brine) by conduction from the food to the refrigerating medium through one or two metal plates or packaging material or both. This might be accomplished by two endless metal belts traveling in the same direction and at the same speed through a tunnel. The calcium chloride brine is sprayed onto the top of the upper belt and underneath the lower belt.

The *multiple-plate freezer* invented by Birdseye is one of the most extensively used types of indirect freezers. It consists of a number of hollow metal plates, usually made of rolled aluminum alloy and mounted so that the space between them is adjustable. The product to be frozen is introduced between the plates on trays holding the boxes of uniform thickness into which food has been packed. The shelves are then moved up-

ward by a hydraulic device until the layers of packages are in intimate contact with the metal plates. Wooden spacer strips placed on the sides of trays will prevent excessive pressure on the packages. The whole set of trays is enclosed in an insulated cabinet, which is now closed, and the refrigerant (ammonia or brine) is circulated through passages in the plates.

There are many other types of quick-freezing equipment in use for the great variety of products now frozen. See also *Dairy products*; *Eggs*; *Fish and shellfish*; *Ice cream and frozen desserts*; *Meat and meat products*. The marketing of frozen foods offers many problems.

Specially insulated cars and trucks refrigerated by mechanical means or with salt-ice freezing mixtures are generally used for the bulk transportation of frozen foods. Dry ice (solid carbon dioxide) is also extensively used, especially for the refrigeration of smaller quantities of frozen food in transit. Temperatures in the range of  $+10$  to  $-10^{\circ}\text{F.}$  are most commonly used for frozen-food storage. By and large, the lowering of the storage temperature from  $10$  to  $0^{\circ}\text{F.}$  will double the storage life of frozen fruit juices, vegetables, most meats, dairy products, poultry, etc.

Frozen foods that have been thawed should not be refrozen. Even foods handled and frozen under ideally sanitary conditions will contain surviving organisms. Because of the destruction of the original cell structure by blanching, freezing, and thawing, bacterial growth is very rapid in defrosted foods. For this reason, thawed frozen foods should be utilized or cooked within a few hours of defrosting. When such products are refrozen, they will be particularly susceptible to spoilage during subsequent defrosting, and the increased bacterial count will also often decrease their nutritional value and eating quality. Thus, the common recommendation against refreezing is a sound precautionary measure.

**Dehydrofreezing** is a process in which the product is partially dehydrated before freezing. This procedure has certain advantages over both dehydration and freezing. For instance, the rehydration and thawing processes can be combined by placing the dehydrofrozen product in boiling water. The storage space required for dehydrofrozen products is less than that needed for the directly frozen commodity. The practical possibilities of this new method seem to be limited as yet because of the higher cost of processing.

The methods used for the preparation of fruits and vegetables for freezing are essentially the same as those applied in canning. Blanching is required for most vegetables in order to ensure sufficiently long storage life.

As an illustration of a commercial freezing process, the preparation of consumer packages of frozen sliced strawberries is given in the following outline:

*Strawberries*—either picked without caps or decapped.

*Washing and sorting*—to remove unripe, mushy, and injured fruit.

*Slicing*—by mechanical slicers into  $\frac{1}{4}$ – $\frac{3}{8}$  in. thick slices.

*Sugaring*—usually in the proportion of either 4:1 or 5:1, meaning the pounds of fruit per pound of sugar.

*Filling*—into cellophane bags standing in rectangular cold-waxed cartons; paper-metal combination boxes for mechanical sealing are now also available.

*Sealing*—cellophane bags by heat; automatic-seal containers by metal tops in closing machine.

*Freezing*—in multiple-plate or other type of freezing equipment.

*Packaging*—usually into corrugated fiberboard boxes.

*Storing*—usually at  $0^{\circ}\text{F.}$  awaiting shipment.

There are a number of different processes used in the production of frozen citrus juices. Usually the strained juice is further screened to separate about 90% of it in a condition essentially free of juice sacs (pulp) which are contained in the other 10%. The 90% portion is then concentrated in multiple-effect high-vacuum evaporators to a somewhat higher degree than required for the finished product. Finally the concentrate is blended with the exact proportion of the 10% fraction containing the pulp to give the whole concentrate, which is cooled, vacuum-packed, and quick-frozen. Sweetening agents are sometimes added, as to lemon juice and one type of orange juice.

**Freezing Lockers and Home Freezing.** Freezing lockers are said to have developed from the good-will gesture of allowing farmers to store food in the corner of freezing plants. This led to the use of boxes and baskets, eventually provided with locks. The modern freezing locker is a sanitary metal cabinet provided with a lock and placed in a room usually maintained at 0°F. Modern community locker plants usually provide special facilities for freezing food and often also for the preparation of the food to be frozen. From a modest start of 250 such plants in the U.S. in 1936, by 1946 the number grew to 8,000 in all states, Alaska, and Hawaii. Beef, pork, poultry, and game make up the bulk of the foods held in community locker plants. The amount of food held by such lockers is difficult to estimate, but, according to the U.S. Department of Agriculture, in 1943, 1,500,000 families with about 7,500,000 persons were served by locker plants with a turnover of some 865,000,000 lb. of foodstuff annually (11). It was estimated that in 1949, 3,300,000 families or 13,000,000 persons were served by locker plants (24).

Home freezing units are in many respects preferable to freezing lockers and commercial or community locker plants, but of course the investment is much higher. The home preservation of most fruits and vegetables is simpler than the processes used in their canning although the need to store under refrigeration presents a continued expense. The fruits and vegetables most commonly preserved by homemakers for their own use are strawberries, raspberries, and peaches, and peas, corn, and asparagus.

#### PRESERVATION BY SALTING AND BY THE USE OF MICROORGANISMS

The proportion of salt present in a food product will determine to a great extent the type of microorganisms that will grow in it. In addition, the presence of salt will also influence the extent of the changes that the microorganisms will be capable of producing. Although salt has been used in food preservation for hundreds of years, its action is not clearly understood. Among the suggested explanations are that salt exerts a poisonous action on certain organisms, that it makes moisture unavailable to microorganisms, that it will prevent bacterial growth by plasmolysis of the cells, and that it destroys bacterial protoplasm. Whatever may be the mechanism of salt action, the fact remains that salt, especially in combination with acids, has a selective action on microorganisms. This effect is extensively used in the manufacture of pickles, sauerkraut, and many other products. Dairy products like butter and cheese and a great variety of fish and meat and meat products are also salted.

There is little doubt that most fermented foods were discovered by accident and there seems to be even somewhat more uncertainty concerning the mechanisms involved in their production than in the case of the preservation methods discussed previously. A few of the major products of this type will be discussed. See also *Fermentation*.

*Sauerkraut* was introduced into the U.S. by German and Dutch immigrants but



it is said to have originated in China (15). In its preparation on a commercial scale, the cabbage shreds are prepared in the manner described under "Dehydration" and then packed into barrels or large wooden or concrete vats having 50-40 ton capacities. During the packing, salt is added to the extent of about 2.0-2.5%, care being taken to achieve even distribution. When the vats are fully packed, they are covered by white muslin cloth and then with a wooden cover, which is weighed down with concrete blocks just enough to cause the juice to rise to the cover but not to flood over it. Now the bacteria present on the cabbage leaves become active, and the temperature will rise but should be kept as near 65°F. as possible. At different stages of the fermentation, different organisms will dominate. Lactic acid and a smaller proportion of acetic acid are the main fermentation products, together with many other compounds formed in smaller quantities. The fermentation is complete in about 10 days. The acidity changes in the juice are carefully followed by daily titrations and, when the acidity reaches 1.6% (as lactic), the kraut is considered ready for packing.

Sauerkraut is often shipped in bulk, but in the U.S. most of it is canned. For canning, the kraut is first warmed, and the shreds are broken apart and filled into the cans, usually by hand. The cans are first exhausted and then processed in boiling water for 10-30 minutes, depending on the size of the can.

*Pickles* are prepared by a great variety of methods, and not all of the products are fermented. Some of the types produced are fermented pickles; unfermented, fresh pasteurized pickles; sweet, sour, and mixed pickles; and many types of relishes.

Cucumbers are harvested in large quantities over a short period of time and therefore must be preserved in some manner for later processing. Since they cannot be satisfactorily canned, frozen, or dehydrated, brining is commonly used. There are two major methods of brining. In the low-salt method, the cucumbers are washed and then placed in an 8% salt solution, with 9 lb. more of salt added for every 100 lb. of cucumbers. The salt used must be low in calcium and magnesium. Then the tanks are closed so that all cucumbers are covered by liquid, and during the following weeks the salt concentration is raised until it reaches about 16%. The salt concentration in brining is expressed in *salometer readings*, based on the solubility of salt. A reading of 100° salometer indicates approximately a 26.5% solution of sodium chloride. In the high-test method, the starting salt concentration is about 10.6% salt solution with further additions of salt as noted above. The timing in increasing the salt concentration is very important. Pickles preserved in 16% salt solution will keep for years. When storage for more than a year is anticipated, the salt concentration is often raised to 18-19%.

The fermentation starts a few days after brining and will continue for several months. Again, a number of microorganisms (including yeasts) participate in the fermentation, and the main fermentation products are acids, ethyl alcohol, carbon dioxide, and other gases, sometimes including hydrogen. The fermented product is known as "salt stock." For processing, the pickles are sorted and the salt is then removed by repeated soaking in water. Alum may be used in the last soaking water to harden the pickles, but in the U.S. such treatment must be declared on the label. The pickles are then covered with distilled vinegar of about 6.5% or weaker and after soaking for 4-10 days they are placed in the final container like barrels or glass jars. A variety of spices are used in the preparation of pickles. For dill pickles, the fermentation is carried out in the presence of dill and spices. Other vegetables like onions, beets, cauliflower, and green and red peppers are pickled and fermented by

similar methods. The processes used for pickling are empirical and many steps in the procedures are not clearly understood.

*Olives* contain a glycoside (oleuropein), which must be destroyed by dilute alkali at room temperature or dilute acid under pressure in order to remove bitterness. The olives for pickling must be harvested at a specific stage of maturity as indicated by color, but this stage is quite different in the olive varieties commonly used. They must often be preserved by salting for later processing. The olives are frequently held in an 8% salt solution, and lactic acid is at times added to prevent spoilage. With longer storage, salt concentrations up to 12% are used. Here, as with other pickled products, it is important to build up the salt concentration gradually. In processing, the olives must undergo several treatments. In the first treatment with dilute (0.5–2.0%) lye (sodium or potassium hydroxide), the color is intensified during the treatment, which might last 24 hours. When the alkali has penetrated the skins to the required depths, the olives are exposed to air for 2–4 days and then treated several times with lye to eliminate the bitterness. The alkali is removed by repeated leaching with water at 120–140°F. until practically all water-soluble constituents are removed and the olive flesh consists mostly of fiber and olive oil (10–20%). After the lye is completely removed, the olives are cured in a 2% brine for about 2 days and then the salt concentration is raised to about 3%. The olives are sorted, graded (for size and color), and packed into lacquered cans. Boiling brine is used to fill the cans, which are next exhausted to a center temperature of 185°F., sealed, processed at 240°F. for 60 minutes, and cooled. In glass packing, the product is pressure-cooled.

#### PRESERVATION BY CHEMICALS

For the chemicals used in food preservation, and for smoking as a method of preservation, see "Preservatives" under *Food chemicals*.

#### PRESERVATION BY IRRADIATION

Ultraviolet light of certain wave lengths has been shown to have bacteriostatic and fungistatic action, and is used to some extent in preventing air-borne infection of various food products. Other ionizing radiations have been used to a limited extent but are mostly in the process of development. It is believed by some that such methods will provide means for food preservation void of the almost universal detrimental effects of present methods on flavor. The high cost of effective treatment and the small extent (depth) of penetration of many types of otherwise suitable irradiations are as yet major difficulties that prevent large-scale application of such methods.

#### Effect of Processing on the Nutritional Value of Foods

For the present discussion the nutritional value of a food might be considered on the basis of calorie value; the ability to supply specific nutrients, as proteins (*q.v.*), amino acids (*q.v.*), and fats (*q.v.*); the presence of various required elements (minerals), including trace elements; and the vitamin content (see *Vitamins*).

The *calorie value* of processed foods (in the ready-to-eat stage) is about the same as that of the corresponding food items (dishes) prepared directly from fresh materials. At times there are slight losses due to leaching, while at other times the calorie value is increased by the use of sugars and other added ingredients.

*Proteins* vary in both chemical composition and in usefulness to satisfy human

requirements. The "biological value" of a protein is in reality a measure of its ability to supply amino acids which the human body requires but cannot synthesize and to provide "dispensable" amino acids to minimize the requirements for the synthesis. A varied diet composed of both plant and animal products is now thought to be required to supply all amino acid requirements. As far as is known at the present time, the loss in protein and amino acids in processing is small, and, in general, processing does not greatly change the usefulness of proteins and amino acids.

Of various *elements* (mineral nutrients) needed by the body, losses occur in proportion to the extent of cooking and leaching to which the food is subjected. The loss will also depend on the solubility of compounds in which the specific element occurs. In general, such losses during heat treatment alone are not great enough to cause concern to the nutritionist, but refining treatment, as in milling, may cause severe losses. It also appears that the methods used in the preparation of foods in the kitchen are often of more importance than processing losses.

The *vitamin* content of processed foods has now been extensively investigated. The results do not justify the prejudice against processed foods, which was noticeable in the U.S. a generation ago, and which is still common in many countries. However, the vitamin losses often are great enough to warrant efforts for improvements.

In *dehydrated foods*, some loss of vitamins will occur, the extent of loss depending mostly on the care exercised in the preparation for dehydration and the process of dehydration applied, and on the period and conditions of storage. The losses in ascorbic acid (vitamin C) are extensive, especially in vegetables.

In *canned foods*, the extent of vitamin losses has been well established. Losses in ascorbic acid occur both in the preparation, especially blanching, and to a lesser degree in processing. Subsequent losses are slight and slow. Any method of preparation that disturbs the natural cell organization, as peeling, cutting, chopping, and puréeing, will tend to increase losses. However, this is fortunately not true in the case of acid products like canned citrus fruit, pineapple, and tomatoes and the juices prepared from these fruits. The high original ascorbic acid contents of these products are for the most part retained in processing and storage. Canning seems to be without detrimental effect on vitamin A and carotene (provitamin A), but losses will occur during storage. Thiamine (vitamin B<sub>1</sub>) is sensitive to heat in neutral mediums and also dissolves easily in water. As a result, losses during canning (and dehydration) are considerable. Riboflavin (vitamin B<sub>2</sub>) is stable to heat in neutral and acid mediums but is soluble in water and thus will be extracted to a certain extent during preparation of foods for canning. This vitamin is labile to light, and its presence in milk accelerates the oxidative destruction of ascorbic acid. Retention of riboflavin during the storage of canned foods is good. Niacin (nicotinic acid) is apparently unaffected by heat in most foods but might be extracted to a certain extent by hot-water blanch. Even during storage at comparatively high temperatures, niacin in canned foods does not seem to be destroyed. Pantothenic acid, pyridoxine, and biotin are easily destroyed in processing. The factors known collectively as folic acid (*q.v.*) seem to be labile to heat and probably are retained to approximately the same extent as thiamine. From the chemistry of vitamin K, it is not reasonable to expect great losses of this vitamin during canning.

In *frozen foods*, the vitamin losses that occur during preparation are the same as in preparation for canning. Subsequent losses will be mostly determined by storage temperatures. The losses of vitamins in most foods stored at 15°F. are significantly

higher than during storage at 0°F. At this latter temperature, frozen vegetables will lose less than 25% of their ascorbic acid content during a period of 6-9 months. The vitamin A and provitamin A (carotene) contents of frozen fruits and vegetables may drop as much as 25% during storage at 0°F. from one season to the next.

It must be realized that these are general statements to which exceptions exist. The situation may be summarized by stating that, once they are dehydrated, canned, or frozen, properly kept processed foods lose their vitamin content slowly. In considering the nutritional value of processed foods, it is only fair to compare them with fresh materials as they are available at the times when processed foods are consumed, rather than with fresh materials in their prime. The long-distance shipping and storage of most fruits and vegetables (that is, those that will withstand such treatment at all), required at some seasons, result in some loss of their original nutritional value; exceptions are citrus fruits, apples, and a few other products. High-quality canned and frozen fruits and vegetables are therefore often superior, not only in quality but also in nutritional value and cost, to the fresh products available during some months of the year.

### Food Packaging

Proper packaging of processed foods is imperative. In dehydrated foods, the product often has to be protected from moisture and oxygen, as well as microorganisms, insects, and rodents. Canned products must be hermetically sealed. Frozen foods have to be packaged to allow proper freezing and to prevent dehydration in storage. In addition to protection and sanitation, proper packaging also provides convenience, economy, and appeal. Here only the major materials used for food packages can be noted. See also p. 846; *Packaging*.

*Paper (g.v.)* is used more than any other material, in the form of bags and envelopes, wrappings, boxes and cartons, liquid-tight containers (as for ice cream and milk), fiber cans, and a variety of others. Dehydrated products are mostly packed in containers, made at least in part of paper. Often multilayer packages composed of cellophane, tin foil, aluminum, etc., in addition to paper, are used. Canned goods are commonly cased in fiberboard boxes. Paper boxes are most commonly used for frozen foods. The metal-end paper container suitable for automatic machine filling and closing is one of the important developments in frozen-food packaging.

*Metal* packages and containers are made out of steel, aluminum, and tin. The most common of these is the tin can, which contains only a small proportion of tin, used for the coating of the steel sheet (see *Metal coating*). Other coatings are also used, often on top of the tin coating. A great many of these coatings (often called lacquers) are based on oleoresinous varnishes. They are usually applied by a roller-coating machine and baked at 250-350°F. for 10-30 minutes. In general, the varnishes contain tung oil and synthetic resins in ratios of 18-30 gal. of oil to 100 gal. of resin. Many different kinds of oils and resins may, of course, be used. See also *Coatings (industrial)* Vol. 4, pp. 149, 164; *Varnishes*. Terneplate and blackplate are steel sheets treated to make them suitable for certain products. Can sizes are designated in various ways, for example, 5Z, No. 1 Tall, No. 303 Cylinder, and No. 2 (the most commonly used size,  $3\frac{7}{16}$  in. in diameter and  $4\frac{9}{16}$  in. high, for vegetables, fruits, juices, soups, and specialties).

Aluminum has now come to the fore as a packaging material. Containers made of

aluminum are at times corrugated to increase their resistance to crushing. Lead (in outer wrappings and laminations), tin, and aluminum are also much used as foil.

*Glass* (*q.v.*) offers some advantages over metal for food containers inasmuch as the product packed in glass is visible. Glass containers are in many ways interchangeable with metal containers and are used very extensively for fruit juices, preserves, and many other products where the color or the condition of the product will attract the purchaser. "Canning," as used today, includes the thermal processing of foods in glass as well as in tin plate.

*Transparent packaging* materials like cellophane, Pliofilm, and many others are extensively used for consumer packaging of fresh, dehydrated, and frozen-food products. The present tendency is to allow the consumer to see the product at least through a "window" made of such materials, wherever this is possible.

*Wood* is still extensively used for packing cases, boxes, baskets, etc.

### **Food Deterioration and Spoilage**

As already noted, it is now clearly recognized that most food materials deteriorate during storage. This is certainly true of fresh and processed fruits and vegetables, fish, dairy products, eggs, etc. Deterioration is usually used to designate a loss of desirable characteristics in a food product, which will not necessarily be unsuitable for human consumption. In contrast, spoilage usually indicates the development of conditions that render food materials unsuitable for human consumption. The line of demarcation between deterioration and spoilage obviously cannot be a sharp one.

**Deterioration** occurs most commonly in the flavor and odor of foods. Off-flavors are perhaps the most common and may be due to many causes. The chemistry of natural flavoring materials is as yet little developed. In the case of fruits and vegetables only a few such compounds have been identified, but in most cases it is clear that the total flavor is composed of many other additional constituents. For instance, it is known that methyl anthranilate is a part of the flavor complex of Concord grapes, yet it is clear that many other constituents, as yet unknown, must make important contributions. From apple juice over twenty compounds of pronounced flavor (mostly alcohols, aldehydes, and esters) have been isolated and identified; yet mixtures of these compounds in the proportions found do not equal the flavor and aroma of apple juice. Even less is known of off-flavors developing in plant products.

A further common type of deterioration is manifested by color changes, almost invariably leading from the typically colored product to one that is more yellow and eventually brown and black. Accordingly, color changes have been classified as primary and secondary, the former indicating loss of natural pigments, and the latter, the development of undesirable colorations. The two reactions are not necessarily inter-related, especially in processed foods. Chlorophylls, anthocyanins, and carotenoids, from which plant foods derive most of their color, are all slowly destroyed by heat. The chemistry of the reactions involved is little understood, with the possible exception of the change of green chlorophylls to yellow or brown pheophytins. Of secondary deteriorative color reactions, the "browning reaction," which occurs in many processed foods, such as dehydrated and canned plant products, eggs, and milk, is perhaps the most important. This group of reactions includes the Maillard reaction between carbohydrates and amino acids, involving the formation of colored reaction products, and many other reactions some of which seem to occur through the intermediary formation of furfural and hydroxymethylfurfural. However, browning is at times

desirable, as in bread crust and roasting. There are a great many other types of deteriorations in all quality factors, including nutritive value.

**Spoilage** is most frequently the result of infection by various types of microorganisms, especially bacteria, yeasts, and molds. It may also be due to enzymic or non-enzymic factors that have caused the product to deteriorate excessively. On the other hand, spoilage may occur without obvious deterioration, and such cases are of most danger from the health standpoint. Bacterial spoilage often leads to *souring* or *putrefaction*, either of which gives warning of the unsuitability of the food for human consumption.

**Food poisoning** is caused by the presence in foodstuffs of toxic materials (other than those added deliberately with criminal intent). The poisons may occur naturally in the foodstuffs or may develop through the action of microorganisms or enzymes; toxic residues of pesticides or metallic contaminants are sometimes also present. Thus, food poisons may be organic or inorganic constituents of plants; animal tissues poisonous to human beings are also known. Again, food poisoning may be caused by the growth in the human body of living organisms introduced with foods as well as by bacterial toxins produced by such microorganisms before or after ingestion. As an example of the former, the presence of typhoid bacteria in certain foods might be cited, while well-known examples of the toxins formed in food are the virulent type produced by botulism organisms (*Clostridium botulinum*) and the staphylococcus toxins. Commercial canning procedures used in the U.S. are now so well controlled that no known cases of botulism from such sources have occurred since 1925. There are known to have been some more recent cases of botulism from home-canned foods where the advice of responsible agencies was not followed, and, in other countries, from food processed commercially under unsuitable conditions.

"*Ptomaine poisoning*" has long since been discarded by modern medical practice as a blanket term used to cloak diagnostic uncertainty (14). Although ptomaines or putrefaction bases, which are relatively simple organic bases, are formed by the action of putrefactive bacteria on protein material, there is no evidence that they cause food poisoning.

The belief that canned foods will become harmful when kept in the open can is also a fallacy. For most canned foods, the can is the best container for the unused portion since it was sterile at the time of opening, while this is not likely to be the case with any dish or pan used. In the case of a few pigmented fruits it is desirable to empty the can since the product is corrosive in the presence of oxygen and the flavor and color of the product might thus deteriorate, but it will not become harmful or dangerous to health on this count.

### Food Supply and Consumption

One of the most obvious trends in U.S. food habits continues to be the consumption of more fruits and vegetables and smaller amounts of potatoes and cereal products. As shown in Figure 1, this tendency has been noticeable for over a generation and became pronounced in recent years (22a). A part of this change is the continued increase in the use of processed fruits and vegetables. Since about 1940, the annual per capita consumption of fresh fruits and vegetables has changed little (+4.4%), but the consumption of processed fruits and vegetables (excluding dry beans) has increased from 55.6 to 83.9 pounds.

The increasing preference given to processed, half-prepared, and prepared foods is due largely to the important savings they offer in the time required for the preparation of meals. There are additional arguments for such food products besides convenience and the relatively small losses during transit and storage (see p. 813). The large-scale preparation of foods is accompanied by much less waste than in home preparation, and the utilization of trimmings and other by-products is only possible in large-scale operations. Processed and prepared foods can be used more completely since the purchaser can obtain quantities nearer to the anticipated needs.

The keen competition in the U.S. resulting from plentiful supplies and high purchasing power leads to considerable emphasis on quality products. This is an important factor in encouraging food producers of all kinds to exert themselves to turn out the best possible product in the most economical manner.

However, not many nations have an abundance of food and even those that have enough are few in number. At the present time, there are only ten countries where

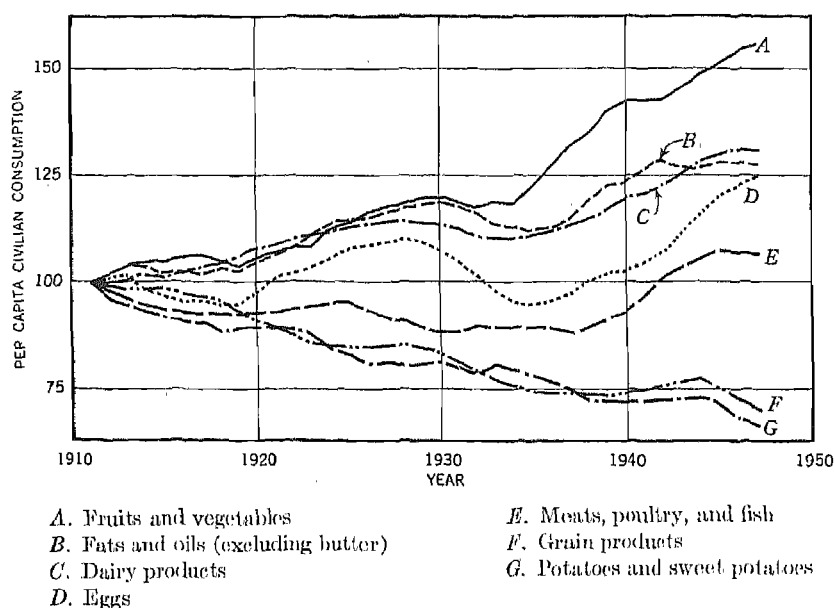


Fig. 1. Trends in eating habits in the U.S. (100 = 1909-13 av.).

the average daily calorie intake per person exceeds the 3000 calories usually set as a minimum for a moderately active man. These are Argentina, Australia, Canada, Denmark, Eire, New Zealand, Norway, Sweden, the United Kingdom, and the U.S. The situation in the U.S.S.R. is not clearly known. According to the latest information (1949), in the Near East and in the rest of Europe the average daily intake is in the range of 2300-2900 calories, while in the Far East (except Thailand) and in all of Africa (except the Union of South Africa) the intake is below 2000 calories.

The extent to which a nation can supply food to its people depends mainly on the following factors: (1) agricultural output; (2) fisheries output; (3) general proficiency in food preservation and processing; (4) conditions of distribution and transport; and (5) individual and collective purchasing power and exchange facilities. The last point is well illustrated by the fact that surpluses of foods normally exist in some countries while in others an adequate diet is lacking.

Past discussions of world-over food-production potentialities commonly led to pessimism and gloom but no action. The so-called "law of diminishing returns" has been often cited to reach the conclusion that, as populations grow, food supplies will not be able to keep abreast. It is estimated that the world's population is now increasing by about 50,000 people daily and will reach 3,000,000,000 by A.D. 2000.

It is clear now that speculations concerning the future of food supplies seldom arrive at conclusions of significance. Population trends cannot be foretold except for the immediate future. Furthermore, in a technological civilization, developments cannot be predicted, even for the immediate future. It is of much more significance, therefore, that for the first time in the history of the human race there is a technical agency charged with the duty of working toward an eventual adequate diet for all. This is the Food and Agriculture Organization of the United Nations (FAO). Some of its goals are increases in the amount of food available through application of present knowledge in improving agricultural production; improvements in food distribution by attacking the economic and financial aspects; and the standardization of methods of nutritional evaluation of foods, statistics, etc.

Another approach to increasing food supplies is the use of radically new methods or different raw materials. The methods that have been used are chemical treatment of natural materials, intentional culturing of microorganisms, and chemical synthesis. Thus both protein yeasts and fats have been produced in large quantities by growing certain molds. In 1943, over one million tons of fodder yeast was produced in Sweden, Norway, and Finland (10). Most of these products need further modification and refinement, yet point the way toward possible major developments in food production. The importance of food yeast is well indicated by the fact that a nationwide conference of research workers and technologists interested in this topic was held in the U.S. in 1948. There are now many synthetic food adjuncts in use (see *Food chemicals*), and synthetic vitamins are used in large quantities. Some synthetic fatty acids (*q.v.*) are now produced, although much work is still needed to make such products entirely suitable for human consumption.

It would seem that the efforts made thus far to increase food supplies by new methods and raw materials, or even to conduct research upon which such developments can be based, have been meager indeed, in spite of the fact that it is now common knowledge that animal proteins and fats can be gained only at the cost of several pounds of carbohydrate feed per pound of product. Major progress in these important fields of future food supplies is not likely to occur until systematic long-term investigations of broad scope are started.

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## FOOD ANALYSIS

The science of food analysis may be divided into two general classifications: *proximate analysis*, in which certain classes of constituents are determined, such as ether extract, ash, volatile material, crude fiber, and proteins; and *ultimate analysis*, in which the concentration of a single element (or, by extension, of a single compound) is accurately established.

There are many reasons for the recent growth and development of this branch of analytical chemistry, but the major ones are among the following: the need for quality control in the standardization and improvement of commercial food products; the development of governmental standards of identity and quality and the prevention of adulteration; and the use by the government of analysis as a basis for determining the amount of taxes or duties on certain foods and beverages (13).

Recent years have witnessed a trend toward increased emphasis on instrumental techniques in food analysis as is evidenced by the many chromatographic and spectrophotometric methods now available (see *Chromatography*; *Color (measurement)*; *Colorimetry*; *Spectroscopy*). It has been claimed recently that 53% of the analytical-laboratory man-hours are used to turn out 9% of the determinations by strictly chemical means. In contrast, the remaining 91% of the determinations were made by 47% of the labor using various physical methods. See also such articles as *Conductometry*; *Density*; *Melting and freezing temperatures*; *Polarimetry*; *Refraction and refractometry*.

### Proximate Analysis

**Moisture.** Due to the fact that the determination of moisture content is a frequently performed operation in the field of food analysis, and that an exact moisture determination on foods is impossible, there are many different methods which attempt to accomplish this purpose. The more important ones are: direct-heating, vacuum-oven, drying over desiccants, immiscible-solvent, the Karl Fischer reagent, and electrical methods (16).

*Direct-Heating Method.* A given amount of material is weighed into a tared dish, which is then placed in a thermostatically controlled oven at 100–135°C. for either a definite time interval or until constant weight is reached. Although at this temperature the loss in weight is actually the loss in total volatile material, it is usually considered to be water.

*Vacuum-Oven Method.* Inasmuch as levulose (D-fructose) breaks down in the presence of water at temperatures above 70°C., the vacuum-oven method is often used in preference to the direct-heating method, especially for foods high in carbohydrates, such as fruit juice, honey, and jams. Samples are accurately weighed into covered dishes, and placed in vacuum ovens operating at 25–100 mm. Hg and maintained at 70–100°C. Drying may be accelerated in some cases by passing a steady stream of dry air through the oven.

*Drying Over Desiccants.* This method is recommended for foods, such as spices, that are high in volatile substances. Samples of food are placed in a vacuum desiccator containing fresh sulfuric acid, and the desiccator is then exhausted to a pressure of not more than 10 mm. Hg. During the first 12 hours the desiccator is rotated 4 or 5 times, and at the end of 24 hours the vacuum is released by allowing air to bubble through the sulfuric acid. The samples are then weighed and replaced in the desiccator containing fresh sulfuric acid, and the process is repeated until constant weight is obtained.

*Immiscible-Solvent Method.* Through the use of the Bidwell-Sterling apparatus and immiscible solvents, such as toluene, xylene, and heptane, a rapid method (about 1 hour) for determining small amounts of water is available. The rapidity of this determination coupled with its ability to differentiate between water and other volatile materials, which would otherwise be computed as moisture, make it very helpful, especially for certain spice products. Samples are weighed into Pyrex flasks fitted with a Bidwell-Sterling tube and condenser. Toluene is added both to the sample and to the receiving arm and distillation is started. As toluene has a boiling point of 110.8°C., water rapidly leaves the sample, is carried into the condenser, condenses, and falls into the receiving tube where, due to its greater density (toluene is 0.866), it displaces some of the toluene in the graduated tube. On completion of distillation, the volume of water in the graduated tube is taken as its weight in grams and the percentage of moisture is calculated.

*Karl Fischer Reagent Method.* Continuous research for more rapid and accurate moisture determinations led to the development of the Karl Fischer reagent method. This test filled a great need especially in testing of the many dried and dehydrated foods used by the armed forces in World War II (17). Provided that the Fischer reagent is standardized often and that interfering substances (those possessing a high-iodine-absorption capacity) are absent, accurate moisture determination can be made in less than 2 hours. Furthermore, by observing due precautions, this method can be used over the entire range of moisture content (that is, from trace quantities to pure

water) using either visual or electrometric-titration procedures. Proper laboratory procedures for the disposal of spent reagents should be followed to avoid undue concentrations of sulfur dioxide.

**Electrical Methods.** Recently, control departments have availed themselves of various rapid electrical methods for determining moisture content of foods. These fall into three general types: (1) Resistance type, depending on the measurement of the differences of electrical resistance in a sample. This varies with the product's moisture content. (2) Dielectric type, based on the fact that the moisture content of a food is directly related to its dielectric constant. (3) Frequency type, based on the measurement of the currents induced in a food placed in the field of a coil through which a high-frequency current flows; the induced currents are dependent on the conductivity of the sample and therefore on its moisture content.

**Other Methods.** One of the more recent methods (19) for determining moisture in dehydrated vegetables involves the addition of water to a weighed sample, lyophilizing the resultant slurry, and completing the drying at room temperature in a vacuum oven or desiccator. Lyophilization accelerates the drying rate so that the final drying is rapidly accomplished and the ultimate dry weight is practically independent of the drying temperature.

Miscellaneous methods include drying *in vacuo* over magnesium perchlorate and the use of vapor-pressure measurements for dehydrated vegetables.

**Ash Determinations.** Ash represents what is left after the organic portion of the food has been burned away. The extent to which single constituents of the ash are determined is rapidly increasing.

**Total Ash.** The analysis of food products for their ash content is usually effected by either of two general methods: In the single-incineration method, samples are first heated usually in platinum dishes at 100°C. to drive off water and prevent spattering. The samples are then inserted in muffle furnaces and heated at 525–650°C. until a white ash is obtained. A little water may be added at this stage to partially dissolve the ash and expose any unburned carbon at the core of the ash. The samples are again dried, re-ashed, and weighed until constant weight is obtained.

The double-incineration technique involves extracting carbonized samples with hot water, filtering, and igniting the filter paper and residue to a white ash. The filtrate is then added to the ash, evaporated to dryness, and ashed to constant weight. Food products high in phosphates or containing even small amounts of lead, arsenic, or antimony should not be ashed in platinum dishes as such dishes become brittle.

**Water-Insoluble Ash.** After weighing the total ash, the water-insoluble ash may be determined by adding water to the total ash, heating it almost to boiling, and filtering through ashless filter paper. After washing, the filter paper and residue are reignited and weighed. The weight obtained represents the water-insoluble ash.

**Water-Soluble Ash.** By subtracting the weight of the water-insoluble ash from that of the total ash, the water-soluble ash may be obtained.

**Alkalinity of Soluble Ash.** After cooling the filtrate obtained in separating the water-soluble ash from the water-insoluble ash, it is titrated with 0.1 *N* hydrochloric acid using methyl orange indicator. Alkalinity is expressed in terms of the number of milliliters of normal acid required to neutralize 100 grams of sample.

**Alkalinity of Insoluble Ash.** An excess of 0.1 *N* hydrochloric acid is added to the insoluble ash, which is then heated to incipient boiling and cooled. The excess hydrochloric acid is then titrated with 0.1 *N* sodium hydroxide using methyl orange. Alka-

linity is expressed in terms of the number of milliliters of normal acid per 100 grams of sample.

In 1949 an improved conductometric method (8) for the determination of ash in white and raw sugar was developed, which was more precise and about 20 times as fast as the conventional ashing method. Through the use of a sugar-ash bridge and a dipping-type conductivity cell, it was shown that the specific conductance was directly proportional to the per cent ash (resulfated ash less 10%).

**Ether Extract or Crude Fat.** Extracts obtained with ethyl ether or other fat solvent contain many types of compounds, such as phosphatides, as well as simple fats (see *Lipides*). The use of the all-glass *Soxhlet fat extraction apparatus* has met with widespread acceptance by food analysts. One of the criticisms of this type of apparatus is that at least 50 ml. of solvent is required for the extraction to proceed, and that usually the extraction is made with recently condensed and consequently cold solvent. Other forms of extraction apparatus include the Johnson, Goldfish, and Underwriters' extractors.

Ground and dried food samples are placed in an extraction thimble, which is then plugged with cotton, placed in a Soxhlet or similar continuous-extraction apparatus, and extracted for 16-48 hours with anhydrous ether or petroleum benzene. The extract is then alternately dried at 100°C. and weighed at 30-minute intervals until constant weight is obtained. However, extractions from products containing volatile ether extracts are transferred to weighed capsules, dried over sulfuric acid, and weighed to determine the total ether extract. The loss incurred by gradual heating to minimum weight at 110°C. represents volatile ether extract, the difference between the total and volatile extracts being the nonvolatile ether extract. Recently, the Goldfish extraction assembly has been receiving widespread attention. Functioning in a manner similar to the Soxhlet apparatus, it requires only 6 hours for extraction, is less fragile, and reclaims a high percentage of the solvent.

The *Roesse-Gottlieb method* is used for most dairy products and also generally for sugars and sugar products. Material is introduced into a Mojonnier tube or similar apparatus, ammonium hydroxide and alcohol are added, and the sample is extracted at least 3 times with ether and petroleum ether. The extracts are evaporated on a steam bath and the residue is dried to constant weight in a boiling-water oven. In dairy products the alcohol serves to precipitate casein, which is then dissolved by ammonia. Petroleum ether serves to make lactose and other nonfatty solids less soluble than would be the case if only ethyl ether were used. A modified form of the Roesse-Gottlieb method, known as the *Mojonnier test*, is now generally employed by industry. Herein the extraction flasks are centrifuged to assist in separating the ether layers; the extracts are then dried in a vacuum oven and cooled in a water-cooled desiccator.

**Crude Fiber.** Foods are analyzed for cellulose, lignin, and a few other constituents, representing materials mostly indigestible by humans. The residues obtained from the ether extraction are digested for 30 minutes with 1.25% boiling sulfuric acid, filtered, and washed. The residue is treated with 1.25% boiling sodium hydroxide for 30 minutes, filtered, washed with boiling water and then with alcohol, and finally dried to constant weight at 110°C. The residue is then incinerated until all carbonaceous material is removed, and weighed; the loss in weight is taken as crude fiber.

**Protein.** Inasmuch as the nitrogen content of different proteins is practically the

same, chemical methods that determine the amount of nitrogen in a food sample will yield results that may be translated into approximate per cent protein. However, some foods (tubers, roots, leafy vegetables, and yeast) contain considerable proportions of nonprotein nitrogen, which will introduce further errors. On the assumption that all proteins contain 16% nitrogen, the factor 6.25 was almost generally used for some time. It is now clear that closer approximation of the true protein content is attained by using different factors for certain products. Some of these are in the range of 5.70–5.95 for various cereal grains and products, 5.18–5.71 for various oilseeds and nuts, 6.38 for milk, and 5.55 for gelatin.

The methods include the *Kjeldahl*, *Gunning*, and *Kjeldahl-Gunning-Arnold methods*. Organic nitrogenous compounds are decomposed by boiling with sulfuric acid, while carbon and hydrogen components are oxidized to carbon dioxide and water. Depending on the method used, copper sulfate, mercury, or selenium may be used as catalyst in this determination, and sodium or potassium sulfate is often added to accelerate the digestion by raising the temperature of the reaction mixture. Simultaneously, with the above oxidation, there is a reduction of a part of the sulfuric acid to sulfur dioxide, which, in turn, reduces the nitrogenous material to ammonia. Reacting with the sulfuric acid, the ammonia forms ammonium sulfate, which, on the addition of sodium hydroxide, releases the ammonia. This is distilled into a known excess of standard acid and back-titrated with standard alkali.

When it is desirable to determine the nitrate as well as the protein nitrogen content of a sample, it is necessary to modify the regular Kjeldahl procedures because ordinarily the nitrate nitrogen is turned into nitric acid and escapes during the digestion. However, by adding an easily nitrated substance, such as salicylic acid, the nitric acid will form the nitro derivative, which after reduction may be converted to ammonia by the usual digestive procedure. The remainder of the determination may then be carried out in the usual manner.

Amino acid nitrogen may be conveniently determined gasometrically by the nitrous acid method of Van Slyke, which is based on the measurement of nitrogen formed from  $\alpha$ -amino acids on treatment with nitrous acid. There is also the gasometric ninhydrin method, in which carbon dioxide released from the carboxyl group of  $\alpha$ -amino acids on boiling with ninhydrin (1,2,3-indantrione hydrate) is measured.

See also p. 823.

**Carbohydrates.** The percentage of carbohydrate material (sometimes called "nifext" for nitrogen-free extracts) in a food is determined by difference, that is, by subtracting from 100 the combined percentages of moisture, ether extract, protein, crude fiber, and ash. This class of substances is usually divided into mono-, di-, tri-, and polysaccharides on the basis of the number of simple carbohydrate groups in their respective molecules. See also p. 824.

The pectin content of plant foods is often defined as soluble and insoluble pectic substances. The former are soluble in cold water, while the latter are insoluble unless treated with acids, ammonium oxalate, or a series of other agents. The pectin content of food products has been commonly determined by the alcohol precipitation method. In this, a solution made from the product is precipitated by the addition of alcohol, filtered off, and then dried. It is clear now that such alcohol precipitates often include other polysaccharides and proteins and therefore estimation by the more exact, although tedious, calcium pectate method is now preferred (see *Pectic substances*).

### Ultimate Analysis

For the determination of carbon, hydrogen, oxygen, etc., see *Organic analysis*.

**Inorganic Elements (Mineral Constituents).** With the recent development of a buffer solution that removes the effect of variable amounts of alkaline earth elements, it is possible to analyze a single sample spectrographically for manganese, iron, aluminum, copper, tin, and lead with an accuracy of 10%. The application of the flame photometer to the field of food analysis in the determination of alkali metals has likewise been of recent origin. In the analysis of foods for single elements, the following developments have been noted:  $\alpha, \alpha'$ -dipyridine is still the preferred colorimetric reagent in the determination of iron; modifications of the dithizone method for the estimation of copper have been introduced; manganese may now be determined microcolorimetrically or microbiologically, the latter by basing the determination on the need of *Lactobacillus casei* for this element.

**Amino Acids (g.v.).** *Chemical and Physical Methods.* Although somewhat overshadowed by recent developments in the advancement of chromatographic and microbiological techniques for the assay of various amino acids, chemical methods have been continually undergoing modifications with resultant improvements in their specificity and sensitivity. There are now reliable colorimetric assay methods for tryptophan, methionine, and isoleucine; ultraviolet absorption spectra form the basis for an estimation of tyrosine and tryptophan; and there are spectrophotometric methods for tryptophan and cystine.

*Chromatographic Methods (see Chromatography).* In recent years, English workers have been credited with the development of the very useful chromatographic methods of amino acid analysis through the use of paper strips and paper sheets (19). After effecting a chromatographic separation in one direction, drying, and then running a second solvent at right angles, two-dimensional separations of amino acids may be obtained. Then by spraying the papers with ninhydrin solution and heating, the position and identification of the individual amino acids may be ascertained on comparison of their loci to those of known controls. The identified amino acids may then be eluted from their zones and quantitatively determined via the microbiological technique. The prominence gained by this method of amino acid assay since about 1945 is largely due to its convenience, speed, and adaptability. It also provides an effective means of separating amino acids from interfering substances, which was not accomplished by other analytical methods. The precision of this method at the present time is considered to be between 10 and 15%.

Of late, there has been experimentation with starch chromatography (19), a method that may prove to be more sensitive but less convenient than the filter-paper technique.

*Microbiological Determinations.* Microbiological methods of assay have undergone considerable improvement despite their relatively recent introduction as an analytical tool. The major difficulty in the preparation of protein hydrolyzates is the avoidance of racemization, or even destruction, of certain amino acids. There have been attempts to improve this situation through the substitution of alkali for acid hydrolysis or even by making determinations directly on the unhydrolyzed material.

As a general rule, there appears to be a preference for methods that require more than one organism for the determination of a series of amino acids in order that greater specificity of response might result from various microorganism requirements as well

as from changes of media and incubation conditions. Typical examples of this technique are illustrated by the use of the following organisms in the assay of one or more amino acids: valine by *Lactobacillus casei*, threonine by *L. fermenti*, proline by *L. brevis*, leucine by *L. arabinosus*, tryptophan by *Tetrahymena geleii*, arginine by *Leuconostoc mesenteroides*, and alanine by *Leuconostoc citrovorum* 8081. However, for those laboratories that do not choose to carry such a wide selection of test microorganisms, there have been developed assay techniques in which a single organism may be used for the determination of several different amino acids. Recently, procedures for the determination of 13 amino acids with *Clostridium perfringens* (Welchii) have been devised (4), as well as an assay method for 9 of the 10 essential amino acids by means of *Streptococcus faecalis* (9).

**Starch and Sugars.** For malt beverages, sirups, extracts, and brewing materials, the simple *iodine-starch reaction* may be used to good advantage as a qualitative test for unconverted starch. However, for cocoa and cereal products, coffee, dessert powders, grain and stock feeds, and spices, one or more of the following standard methods are recommended: gravimetric, polarimetric, and hydrolytic (by means of acid or diastase). A recently developed method requiring not more than a 250 mg. sample for the determination of starch in dried plant materials involves extraction with perchloric acid, precipitation as starch iodide, breakdown of the complex, acid hydrolysis of the starch, and determination of glucose by the volumetric procedure of Somogyi (19). At the present time, work is continuing for more satisfactory methods that can be used for the differential determination of the linear and branched-chain components of starch (*q.v.*).

For specific analytical methods on the determination of mono-, di-, and trisaccharides and for tests for the common sugars, see *Sugar analysis*.

**Vitamins.** Procedures for determining vitamins comprise physical, chemical, biochemical, and biological (including microbiological) methods. See *Ascorbic acid*; *Biotin*; *Folic acid*; *Inositol*; *Nicotinic acid and nicotinamide*; *Pantothenic acid*; *Riboflavin*; *Thiamine*; *Vitamins*.

### General Classes of Foods and Their Important Analytical Tests

**Baking Powder and Allied Chemicals** (see *Baking powders*). *Carbon Dioxide.* Inasmuch as baking powders are used as leavening agents, the determination of their content of available carbon dioxide is of major practical interest. This is obtained by subtracting the residual carbon dioxide from the total carbon dioxide. Total carbon dioxide may be determined gravimetrically with the Knorr apparatus; this method is based on the liberation of carbon dioxide by acid, followed by drying and absorbing the gas in caustic alkali. In the Chittick gasometric method for total carbon dioxide, the amount of carbon dioxide liberated after treatment with sulfuric acid is measured and converted into percentage by weight. Following an initial heat treatment, which releases readily available carbon dioxide, residual carbon dioxide is determined in the same manner as total carbon dioxide.

*Starch.* Official tests include: (1) A direct inversion method, which involves acid hydrolysis and measurement of the resulting dextrose either by the Munson-Walker or Allihn gravimetric method. This method is applicable only to baking powders that are free of calcium. (2) An indirect method, necessary for preparations containing calcium, involves pretreatment with cold hydrochloric acid to remove calcium, which, if present, would lead to erroneously high results. The determination is then carried out according to the direct inversion method.

*Tartaric Acid.* Total, free, and combined tartaric acid determinations may be made on a single sample using the Hartmann method. This technique involves the treatment of aliquot solutions of the sample—one with potassium hydroxide and the other with sodium hydroxide. The solutions are treated with ethyl alcohol and the precipitates are collected and titrated. By applying these results in certain formulas, percentages of free, combined, and total acid may be determined.

**Aluminum.** Although formerly quite common, baking powders compounded with sodium aluminum sulfate (soda alum) are only infrequently encountered today. Determinations of aluminum and sulfuric acid should show amounts equivalent to those found in soda alum. The presence of aluminum may be established qualitatively by the formation of a red aluminum lake on reaction of a solution of aurintricarboxylic acid, baking powder, hydrochloric acid, and ammonium acetate. Aluminum may be determined quantitatively by treating solutions of the ash of a sample with phenylhydrazine, which precipitates aluminum as phosphates.

**Miscellaneous Tests.** Other tests used in the analysis of baking powders and allied chemicals include: determination of neutralizing value, insoluble ash, calcium, potassium, sodium, arsenic, ammonia, and phosphoric and sulfuric acids.

**Alcoholic Beverages.** This section includes certain tests that are common to one or more of the following beverages: distilled liquors, malt beverages, and wines. See also *Alcoholic beverages, distilled*; *Beer*, Vol. 2, p. 409; *Wines*.

**Specific Gravity.** Used for all alcoholic beverages, this determination is easily carried out through the use of a pycnometer by comparing the weights of equal volumes of the sample beverage and water.

**Alcohol Content.** Similar procedures are used for determining the percentages of alcohol by weight and by volume for all alcoholic beverages. In the case of wines, the immersion refractometer may also be used. Before the determination, all carbon dioxide must be removed from sparkling and malt beverages, and it is also necessary to neutralize those wines containing abnormal amounts of acetic acid. In the determination of the percentage of alcohol by volume, known volumes of samples are transferred to distilling flasks fitted with accurate pycnometers as receiving flasks. Water is added and upon completion of distillation the specific gravity of the distillate may be obtained and converted into the corresponding percentage of alcohol by volume by means of reference tables.

**Ash.** The ash content of alcoholic beverages may be accurately determined by either the method of single or double incineration.

**Reducing Sugars.** The Munson-Walker method may be used for the determination of reducing sugars in both wines and malt beverages. In preparation of beer samples, it is first necessary to remove carbon dioxide, while wines must be neutralized, dealcoholized by evaporation, treated with neutral lead acetate, filtered, and freed from the excess lead with dry sodium oxalate. In the actual determination, the reducing-sugar solution is combined with the Soxhlet modification of Fehling's solution, carefully heated, and the reduced copper is filtered off, dried, and weighed as cuprous oxide. The values for concentrations of reducing sugars may then be established by reference to established Munson-Walker tables.

**Sucrose.** Tests are made on wines and distilled liquors either by polarization measurements before and after inversion with invertase or by measuring reducing sugars before and after inversion according to the Munson-Walker method.

**Total Acids.** The natural color and the presence of carbon dioxide in wines and malt beverages makes the ordinary titrations with standard alkali difficult. Carbon dioxide is generally removed by boiling before titrating. The use of azolitmin indicator in the titration of wines and potentiometric titrations to pH 8.2 for malt beverages attempt to overcome some of the inherent difficulties.

**Volatile Acids.** Inasmuch as acetic acid is the major constituent of the volatile acids in alcoholic beverages and as it is found in appreciable quantities only in spoiled wines, this test has practical significance. For wines and malt beverages, the procedure is to steam-distill the samples for specified times, followed by rapid titration of the distillate using phenolphthalein indicator. Results are expressed as grams of acetic acid per 100 ml. of sample.

**Methanol.** Analysis for methanol assumes importance when the samples are suspected of being recovered ethyl alcohol denatured with methanol. The modified Denigès method utilizes the Schiff reagent, potassium permanganate solution, and an oxalic-sulfuric acid solution. Color developed in the sample is compared to that in known standards or may be measured more accurately by the use of a neutral-wedge photometer.

**Other Tests.** Distilled liquors are usually also tested for esters, aldehydes, furfural, artificial colors, total solids, phosphoric acid, and benzaldehyde. Malt beverages are tested for dextrin, protein, carbon dioxide, unconverted starch, and sulfur dioxide. Wines are tested for tartaric acid, glycerol, caramel, tannin, and preservatives.

**Nonalcoholic Beverages.** Carbonated beverages (see Vol. 3, p. 122) and concentrates are included in this group. Methods of analysis correspond to those previously described for alcoholic



beverages with regard to the following tests: specific gravity, alcohol, sucrose, reducing sugars, total acidity, and volatile acids. In addition to these, analyses might be made for citric, malic, or tartaric acids, anthranilic acid esters, preservatives, and artificial sweeteners.

**Cacao and Cacao Products.** See Vol. 3, p. 914.

**Coffee and Tea.** *Coffee.* To test for *caffeine*, samples are extracted with ethyl alcohol in a continuous-extraction apparatus; the extract is then treated with magnesium oxide, hydrolyzed with sulfuric acid, and extracted with chloroform. The chloroform in the extracts, after treatment with potassium hydroxide, is evaporated, and the residue is dried at 100°C. and weighed as anhydrous caffeine. (See also Vol. 2, p. 744.) Analyses for ash, soluble solids, crude fiber, starch, total and volatile acidity, etc., are conducted according to the usual methods. Inasmuch as there is little or no adulteration of coffee in the U.S. (see Vol. 4, p. 222) at the present time, it is felt that the cup tests for determining the acceptability of coffee blends is as important as any other quality test. Due to the extremely hygroscopic nature of *soluble coffee*, the analysis for moisture is an important determination. The samples are dried at 105–110°C. for 5 hours or more at a pressure not exceeding 100 mm. Hg and then can be analyzed in a manner similar to that for roasted coffee. Coffee may also be tested for chlorides, petroleum ether extract, and coating and glazing substances.

*Tea (q.v.).* After steeping in water, the tea leaves will unfurl and macroscopic examination may be made of their structure, as well as for the presence of *dust*, *stems*, and *foreign leaves*. In *water extraction*, tea samples are boiled in a flask fitted with an air condenser, made up to a standard volume, and filtered. Aliquots are evaporated to dryness in a steam bath, oven-heated at 100°C., and weighed. Other tests include determinations of moisture, ash, crude fiber, and caffeine (see above), petroleum ether extract, tannin, and facing material.

**Cereal Products.** This group of foodstuffs includes: wheat flour, rye, oats, corn, buckwheat, rice, barley, soybean flour, bread, baked products other than bread, fig bars and raisin-filled crackers, macaroni, egg noodles, and similar products.

**Moisture.** In general, the moisture-content test for these products may be carried out by either of two standard procedures: (1) the vacuum-oven method, in which the samples are dried to constant weight (about 5 hours) in an oven at a partial pressure of 25 mm. Hg or less; or (2) the air-oven method, which employs a drying temperature of 130°C. for only 1 hour. Results of the latter, faster method closely approximate those of the vacuum-oven method. Due to the high levulose content of fig bars and raisin-filled cookies, samples of these are first mixed with sand and water. After preliminary heating on a water bath, the samples are dried in a vacuum oven for about 16 hours at 70°C. under pressure not exceeding 50 mm. Hg.

In Canada, the Brown-Duvcl method is official. This method involves heating the grain samples in oil and distilling the moisture over into a graduated receiver. Another method uses the Brabender moisture tester. Samples are dried for 1 hour in an oven held at 130°C., weighed within the oven, and the percentage of moisture indicated automatically by means of a dial system.

**Ash.** Samples of all cereal products may be similarly analyzed for ash. Samples are weighed into preignited, weighed ashing dishes, incinerated at 550°C. to constant weight, cooled in a desiccator, and weighed.

**Crude Fiber.** See p. 821.

**Hydrogen-Ion Concentration (q.v.).** Equally acceptable are the colorimetric method using sulfonephthalein indicators and the electrometric method using any standard pH instrument.

**Protein.** Nitrogen determinations may be made by the Kjeldahl, Gunning, or Kjeldahl-Gunning-Arnold methods. With the exception of rye, oats, corn, buckwheat, rice, and barley, where the factor 6.25 is employed, the conversion factor of 5.7 is used to obtain the percentage of protein. The important protein fractions of cereals may be further established by means of their solubility or insolubility in such solvents as 70% alcohol, 5% potassium sulfate, and 1% sodium chloride.

**Fat Acidity.** The following method is applicable to all cereal grains and flour. After extraction of the ground samples with petroleum ether, the solvent is evaporated on a steam bath. The residue is then dissolved in a benzene-alcohol-phenolphthalein solution and titrated with potassium hydroxide. This test is important in indicating the amount of deterioration that these products have undergone in storage.

**Diastatic Activity of Flour.** Prepared flour samples are properly digested for 1 hour at 30°C., subjected to sodium tungstate precipitation, and filtered. Potassium ferrieyanide is added to aliquots, which, after being heated on a water bath, are titrated with sodium thiosulfate in the presence of potassium iodide and starch. The reducing sugars formed by action of the amylases (diastases

in the flour extract reduce the ferricyanide to ferrocyanide. Percentages may be established from reference tables.

**Other Tests.** Analysis is also made for iron, calcium, crude gluten, lipides, carotene, petroleum ether extract, chlorine in fat of flour, citric acid, sugars, sterols as cholesterol, and tartrazine.

**Coloring Matters.** Coloring materials may be divided into two major classes, natural and artificial colors. Natural colors include such animal and vegetable colors as anthocyanins, flavones, carotene, annatto, caramel (see Vol. 2, p. 825), turmeric, chlorophyll, and cochineal. The artificial colors include those coal-tar dyes whose use is permitted in the food industry (see Vol. 4, p. 287). Detailed procedures for the separation and identification of these coloring materials will be found in the methods of the A.O.A.C. (3).

**Dairy Products.** This section includes some of the more important tests on the following dairy commodities: milk, cream, evaporated milk, sweetened condensed milk, dried and malted milks, butter, cheese, and ice cream and other frozen desserts.

**Specific Gravity.** The specific gravity of milk is determined by means of a standard hydrometer (the Quevenne lactometer or the N.Y. Board of Health hydrometer) or through the use of a pycnometer. The determination of specific gravity and fat content makes it possible to approximate closely, by formula, the total solids of a given sample.

**Acidity.** Milk samples are diluted and titrated with standard alkali using phenolphthalein indicator. Results are expressed as percentage lactic acid.

**Total Solids.** Samples of milk or cream (evaporated and sweetened condensed milks must first be diluted) are weighed into tared dishes, heated on a steam bath, and further heated to complete dryness in an air oven at 98–100°C.

**Moisture.** Analyses for moisture content are generally carried out on butter, cheese, and dried and malted milks. Butter samples are weighed into flat-bottomed dishes and dried to constant weight in a boiling-water oven. Cheese and dried- and malted-milk samples are weighed into dishes fitted with covers and dried to constant weight at boiling-water temperature in a vacuum oven under partial pressure not exceeding 100 mm. Hg. Dried air is passed through the oven during the drying process; the dish is covered before cooling and weighing.

**Fat.** The Babcock centrifugal method is generally used for milk and cream, and the Roesse-Gottlieb gravimetric method or its modification in the Mojonnier test (see p. 821) for all other dairy products except butter. The Babcock test for cream and milk depends on the digestion by sulfuric acid of charges of milk or cream in specially designed test bottles. By means of centrifuging and appropriate additions of water, the fat is made to rise into graduated necks of test bottles, where, after temperature adjustment, the percentage of fat by weight can be read off directly (see Vol. 3, p. 508). The fat content in butter is commonly determined according to the modified Kohman test. After driving off moisture from a weighed sample of butter at temperatures not greater than 300°F. and determining its percentage composition, the residue is extracted twice with petroleum ether. The resultant curd is then carefully dried and weighed. From the results of the moisture and curd determinations, the percentage of butterfat in the sample may be calculated.

**Added Water.** Whether or not water has been added to milk may be established by measuring the freezing point or by measuring the refraction of the serum. Because the range for the freezing point of milk is relatively constant, a higher freezing point indicates that water has been added. This measurement is conveniently carried out in a Hortvet or similar cryoscope. The serum measurements are based on Zeiss refractometer measurements of the serum and ash of samples prepared according to the acetic serum, sour serum, or copper serum methods. Variance from established refractometer readings indicates added water.

**Sediment Test.** Well-mixed pint samples of milk are strained through a suitable sediment tester fitted with a standard cotton disk placed over a 1-in. opening. The disks are then compared with standard disks and rated.

**Phosphatase Test.** This test will indicate whether milk has been properly pasteurized or whether raw milk has been added to properly pasteurized samples (see Vol. 4, p. 788).

**Vitamin D.** The rat bioassay line test is still the official procedure for determining the amount of vitamin D in enriched milk.

**Protein in Dried or Malted Milk.** The Kjeldahl-Gunning-Arnold technique is followed using a conversion factor of 6.38.

**Microscopic Examinations.** Both malted-milk products and butter commonly undergo this type of examination. Comparison of suspected samples of either product with known standards will readily reveal the presence of adulterants.

**Salt.** After 10–15 extractions of butter samples with hot water, the amount of salt can be determined by titration with standard silver nitrate using potassium chromate as indicator.

**Coloring Matter.** Ethereal solutions of butter or ice cream are introduced into separate test tubes containing sodium hydroxide or hydrochloric acid. If vegetable colors are present, the hydrochloric acid solution will remain colorless and the alkaline solution will turn yellow. If azo dyes are present, the acid tube will turn pink or red, while the sodium hydroxide solution will remain colorless. Positive identification may then be carried out as indicated by the A.O.A.C. (3).

**Foam Test.** Differentiation between butter and margarine can be made by heating samples over a low flame. Margarine and renovated butter spatter and bump while butter foams smoothly.

**Weight for Unit Volume of Packaged Ice Cream.** Packaged samples of ice cream are unwrapped, weighed, and placed in containers full of kerosene. After computing the volume of displaced kerosene, the weight per unit volume of the ice cream as pounds per gallon may be determined from a formula.

**Gelatin.** This test may be used to detect the presence of gelatin in milk, cottage cheese, or ice cream. Samples are prepared, treated with acid mercuric nitrate solution, and filtered. Aqueous picric acid is added to the filtrate and the presence of considerable gelatin is established by the appearance of a yellow precipitate, although smaller amounts might show up only as a general cloudiness.

**Eggs and Egg Products** (see also Vol. 5, p. 476). **Total Solids.** Samples are weighed into previously dried, tared, covered dishes and are heated to constant weight at 98–100°C. in a vacuum oven at 25 mm. Hg or less.

**Lipides and Lipoid Phosphoric Acid.** The analyses of eggs for these constituents characterize egg products better than tests for most other constituents. Total lipides are determined by extracting samples first with a chloroform–ethyl alcohol mixture and then with chloroform. Filtrates are evaporated and the residues are dried to constant weight at 100°C. Lipoid phosphoric acid is determined by dissolving lipide samples in alcoholic sodium hydroxide, drying, and heating at 500°C. The ashes are treated with nitric acid and filtered, and phosphoric acid determinations (as  $P_2O_5$ ) are made on the filtrates.

**Dextrose and Sucrose.** Samples are extracted with sodium chloride solution and ethyl alcohol and filtered, and protein of the filtrate is precipitated with phosphotungstic acid. The filtrate is made up to volume and excess phosphotungstic acid is precipitated with potassium chloride. Corrections should be made for error due to the volume occupied by the precipitate in samples containing added sucrose. Dextrose content of the samples is determined according to the Munson-Walker method on aliquots of the filtrate obtained from the potassium chloride precipitation of phosphotungstic acid. The analysis for sucrose is carried out on the same filtrate by subtracting the amount of dextrose originally present from the amount of reducing sugars present after inversion of the sucrose.

**Acidity of Ether Extracts.** Samples of both liquid and dried eggs are dried to constant weight in a vacuum oven at 55°C. and then extracted in a Knorr apparatus with anhydrous ether. After evaporation of the ether, the extract is again dried in a vacuum oven, weighed, and dissolved in benzene. The samples are titrated with sodium ethylate with phenolphthalein as indicator.

**Ammonia Nitrogen.** This analysis and the acidity of the ether extract serve to point out the amount of deterioration that has taken place. Ammonia nitrogen is easily determined by means of an aeration train in which ammonia-free air is passed through a mixture containing the egg samples, alcohol, sodium fluoride, and sodium carbonate. The air carries ammonia present in the sample into standard sulfuric acid solution, where the excess acid is determined by back-titration with standard alkali.

**Miscellaneous Tests.** Recently, it has been stated that the presence of uric acid in eggs may serve as an index of the amount of chicken manure originally present on the eggs. In addition, the measurement of succinic acid and water-insoluble fatty acid contents of dried or frozen eggs has been claimed to be indicative of their degree of decomposition.

**Organoleptic Tests.** Although the above chemical tests for quality are necessary and do serve a useful purpose, organoleptic testing by means of tasting and smelling is still the final authority in determining the overall acceptability of these products.

**Fats and Oils (1,2,3).** **Moisture and Volatile Material.** Samples are dried to constant weight at 120–125°C. in a vacuum oven at 100 mm. Hg. Constant weight is attained when successive dryings for 1-hour periods show an additional loss of not more than 0.05%.

**Specific Gravity.** The official method determines the ratio of the weights of equal volumes of water and fat or oil as measured in a standard pycnometer at 25°C. Faster but less accurate methods make use of the hydrometer or Westphal balance.

**Index of Refraction.** This factor is conveniently determined by means of either the Abbé or Zeiss butyrefractometer.

**Melting Points of Fats and Fatty Acids.** The two available methods are the Wiley disk and the capillary-tube methods. In the Wiley method, solidified disks of the sample fat are suspended in a cold ethyl alcohol-water mixture having the same specific gravity as the fat. As the temperature of the mixture approaches the melting point of the sample, the fat disk shrivels, and finally becomes spherical at its melting point. The capillary method involves the introduction of melted samples into capillary tubes, sealing one end of the tube, and solidifying the fat by chilling. The tubes are gradually heated in a test tube immersed in a water bath. The melting point is considered to be that temperature at which the fat becomes transparent.

**Iodine and Saponification Values.** See *Fats and fatty oils*; *Fatty acids*.

**Cold Test.** This analysis is to determine the adequacy of winterization treatment of oils. Samples of oil are immersed in a mixture of ice and water for a period of 5 hours and then examined for the presence of precipitated material.

**Stability Tests (Swift and Schaal) and Rancidity Test (Kreis).** See *Fats and fatty oils*.

**Fish and Marine Products** (see also *Fish and shellfish*). **Total Solids.** Only oysters, clams, mussels, and scallops are analyzed for total solids. Samples are weighed into metal dishes, evaporated on steam baths, and dried 4 hours in a water oven at 98–100°C.

**Salt.** To appropriate-sized samples are added known volumes of standard silver nitrate solution in excess of the amount needed to precipitate all chlorides as silver chloride. After digestion of the samples with boiling nitric acid, the excess silver is titrated with standard ammonium thiocyanate in the presence of ferric ammonium alum indicator.

**Quality Tests.** Although the physical appearance and organoleptic tests for fish quality are still of primary importance, they are rightfully supplemented by such objective chemical tests as those for ammonia, indole, and trimethylamine.

**Ammonia.** The use of the Folin aeration train involves drawing ammonia-free air for 3–6 hours through ground samples of fish suspended in water and ethyl alcohol to which sodium carbonate has been added. Ammonia liberated from the samples is carried into flasks containing known volumes of standard acid. After aeration is complete, excess acidity is back-titrated with standard alkali.

**Trimethylamine.** The most satisfactory method for detecting spoilage in sea fish is claimed to be the estimation of the trimethylamine content. Fish samples are made alkaline with potassium carbonate, extracted with toluene, and mixed with picric acid reagent. The formation of the yellow picrates may be measured colorimetrically (7) and compared to known standards.

**Flavorings.** **Vanilla Extract and Substitutes.** The alcohol content by volume is determined in a manner similar to that given for alcoholic beverages (see p. 825). To test for *vanillin*, vanilla samples are treated with lead acetate solutions and then filtered. Aliquots of the filtrates, as well as standard vanillin solutions, are treated with phosphotungstic-phosphomolybdic reagent and, after filtering, the developed blue colors are compared in a colorimeter. Two recognized procedures for determining *lead numbers* are the Winton and the Wichmann methods. In the Winton method, samples of vanilla extracts are evaporated in water baths at 70°C. or less and then treated with neutral lead acetate solution and filtered. Residual lead in the filtrate may be determined as lead sulfate or chromate and the results reported as lead number (Winton). To test for *vanilla resins*, vanilla extracts are evaporated, acidified with hydrochloric acid, and filtered. The resin residue is then dissolved in ethyl alcohol and dried to constant weight at 100°C. To determine the *color value*, aqueous alcoholic solutions of vanilla extracts are prepared, and red and yellow color values are measured in a Lovibond tintometer.

**Oils of Lemon, Lime, or Orange in Oil-Base Flavors.** Samples are measured into Kjeldahl flasks and steam-distilled into graduated Wilson receiving flasks. Upon completion of the distillation, the volume of oil can be read off directly and converted into per cent by volume of the sample.

**Citral.** Samples of orange or lemon extracts are made up to known volume with ethyl alcohol. Aliquots are transferred to colorimeter tubes, *m*-phenylenediamine hydrochloride-oxalic acid reagent is added, and the resulting color compared to that of standard citral solutions.

**Benzaldehyde.** Duplicate samples of almond extract are treated with phenylhydrazine solution and filtered. After washing the precipitates with water and ethyl alcohol, they are dried at 70°C. and converted into weight of benzaldehyde per 100 ml. of sample.

**Ginger.** Samples are partially evaporated and extracted with ether. Upon evaporation of the ether, sulfuric acid and vanillin are added. If ginger is present, a blue color will develop.

**Methyl Salicylate.** Any methyl salicylate present in samples is converted into potassium salicylate by heating with potassium hydroxide. Excess hydrochloric acid is then added and ether extractions made, which are filtered, evaporated, and dried in a desiccator containing sulfuric acid. The weight of the salicylic acid is converted into percentage by volume of methyl salicylate in the sample.

**Fruits and Their Products.** *Moisture.* The standard vacuum-oven method is used (see p. 819).

*Soluble Solids.* By means of a refractometer, the soluble solids of samples may either be computed or read off directly. When insoluble material is present, the refractometer readings must be corrected in determining the final percentage of soluble solids.

*Titrateable Acidity.* Prepared fruit or fruit juice solutions are diluted with boiled water and titrated with standard alkali using phenolphthalein as indicator.

*Sucrose.* This is determined by polarizing sample solutions before and after inversion or by determining the amounts of reducing sugar before and after inversion.

*Reducing Sugars.* Determinations are made according to the Munson-Walker method as used for alcoholic liverages (see p. 825).

*Benzoic Acid.* Although preliminary treatments of different classes of fruit products vary, samples are treated with a saturated salt solution to precipitate protein and other extraneous material. Aliquots of the filtrate are transferred to separatory flasks, progressive extractions are made with chloroform, and the extracts are evaporated to dryness. The residues are dissolved in neutral ethyl alcohol and titrated with standard alkali using phenolphthalein as indicator.

*Total Sulfurous Acid.* Using the Monier-Williams method, food samples are introduced into flasks containing hydrochloric acid and fitted with reflux condensers. Samples are boiled in a slow current of carbon dioxide with the freed sulfur dioxide passing into a solution of hydrogen peroxide. When distillation is complete, the solutions are titrated with standard alkali using bromophenol blue as indicator.

*Other Tests.* Analyses are also made for alcohol precipitate, volatile acids, lactic acid, phosphoric acid, dextrose, gelatin, agar, and sweetening substitutes.

**Meats and Meat Products** (*q.v.*). *Added Water in Sausage.* Samples are weighed into tared weighing bottles and dried at 101–102°C. for 16–18 hours, or at 120–130°C. for 2–3 hours. Total nitrogen is determined by any of the Kjeldahl tests and the percentage protein is determined by multiplying by the factor 6.25. Added water is equal to the difference resulting from subtracting 4 times the per cent protein from the per cent moisture.

*Salt.* Samples are ashed in the presence of sodium carbonate solution, extracted with water, and filtered. Residue is reignited and dissolved in nitric acid, filtered, and added to the previous water extract. A known volume of silver nitrate in slight excess is added, and the precipitate is filtered and washed. Ferric indicator is added to the filtrate and the excess silver is titrated with thiocyanate.

*Crude Fat.* Standard methods are used (see p. 821).

*Ammonia.* The procedure is the same as that used for fish (see p. 821).

*Starch.* If strongly positive qualitative results are obtained upon the addition of iodine solution to aqueous suspension of meat samples, quantitative analyses should be made. Meat samples are dissolved in alcoholic potassium hydroxide by heating on a steam bath, ethyl alcohol is added, and the material is filtered. Sulfuric acid is added to the residue, which after heating is treated with phosphotungstic acid; the material is then filtered, the filtrate neutralized, and its dextrose content determined according to the Munson-Walker method (see p. 825).

*Soybean Flour.* After digestion in alcoholic potassium hydroxide, meat samples are made up to volume in sedimentation tubes with ethyl alcohol. The residue after decantation is washed, centrifuged, and examined microscopically using polarized light for the presence of characteristic hour-glass-shaped cells.

*Soluble and Insoluble Nitrogen.* Meat samples are successively extracted with ammonia-free water, filtered, and made up to volume. Soluble-nitrogen determinations may then be made on aliquots of the filtrate by either of the usual three methods of determining nitrogen (see p. 822). Upon determining the total nitrogen in the meat samples, the insoluble nitrogen may be ascertained by subtracting soluble nitrogen from total nitrogen.

*Meat Bases.* This value is obtained by subtracting from the percentage of total nitrogen the sum of the percentages of nitrogen in insoluble nitrogen, coagulable nitrogen, proteose, peptone, and gelatin. This result multiplied by the factor 3.12 gives percentage of meat bases.

**Sulfur Dioxide.** This determination is done according to the Monier-Williams method as given for fruits and their products (see p. 830).

**Other Tests.** Analyses are also made for nitrates, nitrites, glycogen, colorings, amino nitrogen, agar, gelatin, creatine, and glycerol.

**Nuts and Nut Products** (see also *Nuts*). **Moisture.** Samples are weighed out, water is added, and samples are dried at 70°C. under a pressure not exceeding 100 mm. Hg.

**Fat and Constants of Fat.** After extracting comminuted samples with chloroform and filtering, aliquots of the filtrate are taken and dried at 100°C. The percentage of fat, refractive index, and iodine value may then be run on the residue.

**Sugar and Salt.** Following extractions of samples with petroleum ether and a chloroform-carbon tetrachloride mixture, the separated residues of sugar and salt are dissolved in water and filtered. The percentage of chlorides is determined on an aliquot of the filtrate by titration with silver nitrate in the presence of dichromate indicator. Sugar is determined in a similar aliquot according to the Munson-Walker method of determining the amount of reducing sugars before and after inversion.

**Organoleptic Testing.** As in the case of most fatty foods, the senses of taste and smell must be relied upon to a large extent in detecting off-flavors and odors or incipient rancidity.

**Other Tests.** Analyses are also made for crude fiber, dextrose, starch, rancidity (Kreis), and glycerol.

**Spices and Condiments.** **Moisture** in spices may be determined either by direct heating or by toluene distillation. In the former method, samples are dried at 110°C. and the volatile ether extract is subtracted from the total loss to give loss due to moisture. In the toluene distillation method, the determination is carried out according to standard procedures (see p. 819).

**Ash.** Most spices are ashed at temperatures of 550-600°C. with sufficient wettings of the ash to be sure that it is carbon-free.

**Alcohol Extract.** Samples are extracted with ethyl alcohol for 24 hours and filtered, and aliquots are evaporated and finally dried to minimum weight at 110°C.

**Starch.** Pulverized samples are extracted with ether and ethyl alcohol and the amount of starch in the residue is determined by treating with amylases, hydrolyzing with hydrochloric acid, and finally ascertaining the amount of reducing sugars according to the Munson-Walker method.

**Crude Fiber.** Standard procedures are followed (see p. 821).

**Volatile Oil.** Samples are transferred to distillation flasks equipped with proper volatile-oil traps, water is added, and the mixture is boiled for 4-8 hours. Results are reported as milliliters of volatile oil per 100 grams of spice.

**Microscopic Examination.** A background of vegetable histology as well as an acquaintance with common spice adulterants is necessary to detect certain forms of adulteration. The reactions of spice mixtures with such chemical reagents as the Schweizer reagent ("cuprammonium hydroxide solution," a solvent for cellulose), Millon reagent for proteins, iron acetate, and alkanet tincture help in the identification of spice components.

**Color in Vinegar.** A Lovibond tintometer is used with results reported in terms of the  $\frac{1}{2}$ -in. cell.

**Caramel in Vinegar.** Samples of vinegar are combined with a tannic acid in sulfuric acid-formaldehyde solution, heated at 100°C., and examined for a brown precipitate.

**Other Tests.** In spice mixtures, tests are made for calcium oxide in ash, tannin, and constants of the volatile oil; in prepared mustard, tests are made for solids, acidity, starch, crude fiber, and colorings; in mayonnaise and salad dressing, tests are made for total solids, total acidity, and total fat gums; vinegar is tested organoleptically, and for solids, total acids, metals, and preservatives.

**Sugar Products.** This section deals with some of the more important tests for confectionery (*q.v.*), honey, and maple sirup. For detailed information, see *Sugar analysis*.

**Moisture.** Samples of honey are dried upon pumice stone or quartz sand at 70°C. or less and at 50 mm. Hg. Maple products may be analyzed for moisture by direct heating at 100°C. or by vacuum drying at 70°C. Any of the above-mentioned methods may be used for confectionery.

**Sucrose.** The sucrose content of these substances may be determined polarimetrically or chemically according to the Munson-Walker method.

**Free Acid.** In the analysis of honey, samples are dissolved in water and titrated with standard alkali using phenolphthalein as indicator.

**Commercial Invert Sugar.** This test is also used for honey; samples are extracted with ether and

resorcinol solution is added to the ether extract. The appearance of a cherry-red color indicates a positive test.

*Ash.* Important in the analysis of maple products, this test may be made by either the single- or double-incineration technique (see p. 820).

*Lead Number.* This test is one of the important tests in the detection of adulteration of maple products. At present, there are two officially recognized lead numbers for maple products, the Canadian lead number and the Winton lead number. The Canadian lead number is easily determined by treating known aliquots of aqueous solutions of maple products with standard basic lead acetate solution. After standing and filtering, the precipitate is dried at 100°C., weighed, and the weight multiplied by 20 to give the Canadian lead number. (See also p. 829.)

**Processed Vegetable Products.** *Total Solids.* Samples are first heated to apparent dryness at 70°C. in a vacuum oven at 450 mm. Hg or less in a current of dry air. Drying is then completed by heating for 4 hours at 70°C. and at a pressure not exceeding 100 mm. Hg.

*Insoluble Solids.* After repeated extractions of samples with hot water, the extracts are filtered through and the residue transferred to weighed filter papers, which after washing are dried at 100°C. and weighed.

*Soluble Solids.* The percentage of total solids less the percentage of insoluble solids will give the percentage of soluble solids.

*Ash.* This test may be carried out by either the single- or double-incineration technique (see p. 820).

*Alcohol-Insoluble Solids in Peas.* Washed canned peas are comminuted and samples are extracted with boiling 80% ethyl alcohol. The extracts are suction-filtered through weighed filter papers, the residues are washed with ethyl alcohol, dried over a boiling-water bath, and weighed.

*Mold Count.* The Howard mold count (3,6) has been successfully employed in the analysis of citrus juices, cranberries, and tomatoes and other products containing tomato sauce. Although the presence of a high mold count may indicate contamination of the products by unclean equipment, it usually points to the use of moldy raw materials. By placing a representative sample of the food material on the Howard cell and adjusting the microscope field to a standard diameter, it is possible to arrive at the mold count or percentage of positive fields in a given sample. As there is a definite relation between the mold count and the percentage of rot by weight, the Food and Drug Administration takes action against food products as being unfit for human consumption if certain arbitrary limits are exceeded (that is, if there are more than 40% positive fields in tomato catsup, purée, or paste, or more than 20% positive fields in tomato juice). The Howard method may be used similarly for the estimation of the number of yeasts, spores, and bacteria in tomato products by use of a blood-counting cell. Excessive numbers of these microorganisms indicate that delays in storage or manufacturing processes have occurred to the point where fermentation has taken place.

*Insect-Fragment Test.* The Wildman adaptation of the Howard method provides excellent recovery of both insects and insect fragments from tomato products, puréed baby foods, berries, meals, flours, and certain dried fruits. For the most part, this method depends upon bringing all parts of an aqueous suspension of a sample into intimate contact with such flotation agents as castor oil, mineral oil, or gasoline. Upon separation of the water-oil layer, the fragments will be found in the oil layer where they may be trapped, filtered off, and counted by means of a microscope. It has been recently claimed that identification of the fragments was improved by reflecting the image on a screen.

*Excretory Contamination.* A simple spot test for urea has recently been devised, which may replace the fluorescent test for rodent urine on bagged commodities (19). By brushing or spraying potential areas with an alcoholic solution of *p*-dimethylaminobenzaldehyde and oxalic acid, contaminated areas will take on a distinct yellow color.

*Other Tests.* Analyses are also made for specific gravity (tomato products), sodium chloride, total acids, and volatile fatty acids.

### Food Standards, Definitions, Standards of Identity, and Specifications

The various U.S. Government, state, and municipal agencies have issued many standards or tolerances in food composition, quality, and grades. In addition, there are many standards for foods and beverages which concern the public health (bacteriological, toxicological, and chemical). The enforcement of these laws and regulations

requires extensive laboratory food analyses. Most government and state agencies such as the Armed Forces, Veterans Hospitals, and large institutions, purchase supplies on specification. Many large corporations purchase foodstuffs by specification, grade, or guarantee that government standards have been met. For example, the U.S. Federal Food, Drug, and Cosmetic Act of 1938 provides for the formulation and issuance of regulations establishing for any food a reasonable definition and standard of (1) identity, (2) quality, and (3) fill of containers. Standards of identity are based on normal composition of the food under consideration. "Tomato juice," for example, is defined as "the unconcentrated strained liquid extracted from mature red or reddish tomatoes with or without scalding, followed by draining. The liquid may be homogenized and may be seasoned with salt." More often a food is standardized through the use of numerical limits to control its composition. Preserves and jams must have at least 45% by weight of fruit ingredients to 55% by weight of optional sweetening ingredients (sugar, dextrose, honey). Color, size, texture, quantity, and freedom from defects provide bases for standards of quality and fill of container. Once a definition and standard of identity for a particular food have been issued, a product must actually conform to the standard promulgated if it is represented to be such a food.

Among the various U.S. Federal agencies having more or less supervision over food are: under the Federal Security Agency, the U.S. Public Health Service (milk control—also policed by the American Association of Medical Milk Commissions—shellfish control, etc.) and the Food and Drug Administration (direct control over imported food and food moving in interstate commerce, authorized by the Food, Drug, and Cosmetic Act and acts covering specific foods); under the Department of Agriculture, the Production and Marketing Administration (inspection and grading), the Meat Inspection Division of the Bureau of Animal Industry, the Bureau of Agricultural Economics (butter and eggs), the Bureau of Entomology and Plant Quarantine (insect infestation of fresh fruits and vegetables), and the Food Distribution Administration (quality standardization); under the Department of the Interior, the Fish and Wildlife Service; the Interstate Commerce Commission; and the Federal Trade Commission. "United States Grades" have been established for a large number of commodities. Various grades and specifications are applied to meats, poultry, eggs, grains, and fresh and processed fruits and vegetables (see also *Bakery processes and products*; *Cereals*; *Dairy products*; *Eggs*; *Food chemicals*; *Meat and meat products*). Generally, all fresh fruits and vegetables are graded; they must be graded if they are to be exported. The top grade is U.S. No. 1, but other designations are also used, as for example in the case of apples: Extra Fancy, Fancy, combination of Extra Fancy and Fancy, and Utility. Specifications have to be drawn up for each particular food, but in general, they are based principally on variety, size and shape, maturity and development, color, permanent grade defects (cracks, scabs, etc.), and condition factors (decay including rots, freezing, etc.). Different designations are used for processed foods (canned, dried, and frozen): U.S. Grade A or U.S. Fancy, U.S. Grade B or U.S. Choice (for fruit) or U.S. Extra Standard (for vegetables), U.S. Grade C or U.S. Standard, etc., based on numerical scoring starting with 85–100 or 90–100 for U.S. Grade A. Not all grades apply to all processed foods, and for some foods there are special grades, as U.S. Grade E (Water Grade or Pie Pack) for canned berries, sweet cherries, and plums. Specifications for processed foods include such characteristics as grade, color, type (as freestone or clingstone peaches), style (as whole or sliced), size or count per container, size and kind of container, and for canned goods, sirup density.



and minimum drained weight. Further information is available from the Department of Agriculture, Production and Marketing Administration, Washington 25, D.C. See also reference (11).

Gross food and beverage adulteration is not so serious as formerly, but constant vigil is required to maintain purity, safety, and quality standards.

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## FOOD CHEMICALS

The use of chemicals in foods often impinges on matters of legal interpretation. It is for this reason that it must be stated clearly that the mention of a particular substance in this article does not in any manner imply approval of the use of that substance in foods. The use of any substance in foods is governed by the various laws and regulations of the Federal, state, or city governments. In particular, the Federal Security Agency, U.S. Food and Drug Administration, by virtue of the Federal Food, Drug, and Cosmetic Act of 1938, as amended and extended from time to time, regulates the use of chemicals in foods through sections 402(a)(1)(2), 402(c)(d), and 406(a)(b), and through the various regulations made under this Act. The latest revision of standards and definitions of foods is known as FD&C, SRA 2 rev., Jan. 1949.

It is to be understood that the opinions expressed in this article do not presume to be the official views of any branch of the Federal, state, or city governments.

Chemicals are added to foods for two principal purposes: nutritional and functional.

**Nutritional Chemicals.** Vitamins and minerals are used in the fortification of foods and condiments. This practice was greatly extended during World War II on the basis of governmental requirements and has been continued on a voluntary basis in many instances. Chemicals are also added to foods and condiments for prophylactic purposes, as in the addition of iodine to salt for the prevention of goiter and vitamin D to milk, to prevent rickets. See *Iodine*; *Vitamins*; etc.

**Functional Chemicals.** The functional purposes for which chemicals are added to foods are related, in general, to the processing of foods, their preservation, or the enhancement of their appearance and flavor. They may be classified in the following manner: preservatives; antioxidants; acidulants; neutralizers and ionic adjusters; firming agents; emulsifiers and stabilizers; humectants; maturation agents; bleaching agents; gas storage; coatings and wrappings; flavors (*q.v.*); sweetening agents (*q.v.*); colors (see *Colors for foods, drugs, and cosmetics*).

For a discussion of the presence of insecticides (*q.v.*), fumigants, fungicides (*q.v.*), rodenticides, and similar pesticides (see *Poisons, economic*) as food contaminants, the presence of metallic and other contaminants of foods, and the deliberate adulteration of foods, the reader is referred to the bibliography.

### Preservatives

In the broadest definition, preservatives may be considered to be chemical agents that serve to retard, hinder, or mask undesirable changes in food. Thus many of the categories noted above can be placed in a major grouping of food preservatives. For the purposes of this discussion, it is preferable to limit the definition of preservatives to those substances that inhibit the growth of microorganisms without necessarily destroying them.

The use of chemicals to preserve food is an old and well recognized procedure. A differentiation has sometimes been made between condiments or "kitchen preservatives" and chemical preservatives. The distinction is a legal one rather than a chemical one. Thus the term preservative in the sense of chemical preservative is defined by the British Food and Drug Act of 1928 as follows:

"'Preservative' means any substance which is capable of inhibiting, retarding, or arresting the process of fermentation, acidification, or other decomposition of food or of

masking any of the evidences of such process; but does not include common salt (sodium chloride), saltpeter (sodium or potassium nitrate), sugars, acetic acid or vinegar, alcohol or potable spirits, spices, essential oils, or any substance added to the food by the process of curing known as smoking."

While preservatives used wisely may serve a useful purpose, they cannot take the place of cleanliness in food processing. The use of preservatives will not improve the quality of inferior material nor will preservatives, once spoilage has set in, enable a processor to make a wholesome product out of a polluted one, for the products of spoilage are still present in the foodstuff and are evidence of its contamination.

Both organic and inorganic preservatives are used. Among the principal organic agents are benzoates, *p*-hydroxybenzoates, propionic acid, and other aliphatic acids and their salts. The principal inorganic agents used are nitrates, nitrites, sulfur dioxide and sulfites, borates, iodates, free chlorine, hypochlorites, and peroxides.

**Benzoates.** Benzoic acid,  $C_6H_5COOH$ , and its sodium and ammonium salts are among the bacteriostatic or germicidal agents most used in foods (see also Vol. 2, pp. 467, 469). Sodium benzoate and benzoic acid are listed as optional ingredients in several definitions and standards of identity promulgated by the Food & Drug Administration. Actually it is the benzoic acid that is the effective agent, since sodium and ammonium benzoate must be used in an acid medium to be useful. The acidity of the medium is significant. For instance, a decrease in pH from 7 to 3.5 may increase five- to tenfold the antiseptic and bactericidal action. It has been shown that benzoic acid, salicylic acid, and sulfurous acid are nearly 100 times as efficient antiseptics in strongly acid solution as they are in neutral solution. With benzoic acid and salicylic acid only the undissociated acid is antiseptic, and the benzoate and salicylate ions have virtually no action on yeast. Benzoic acid is more effective against yeasts than against molds. It is customarily used in concentrations of less than 0.1%. The introduction of a side chain (as in phenylbutyric acid) or of substituents such as the hydroxyl group in the para position increases the bacteriostatic action.

Benzoic acid forms a eutectic mixture with water, f.p. about 31.9°F., and contains about 0.16% of the preservative. In this ice the benzoic acid is distributed uniformly. It has been employed as a preservative for fish.

***p*-Hydroxybenzoates.** The esters of *p*-hydroxybenzoic acid have been widely used as food preservatives in Germany and are used as preservatives for cosmetics in the U.S.

**Vanillic Acid Esters.** The esters of vanillic acid (4-hydroxy-3-methoxybenzoic acid),  $CH_3O(OH)C_6H_3COOH$ , have been shown to have preservative action and have been recommended for use in foods.

**Aliphatic Acids.** Most of the fatty acids containing from 1 to 14 carbon atoms are effective mold inhibitors. *Propionic acid* (*q.v.*),  $CH_3CH_2COOH$ , and its sodium and calcium salts have been particularly favored for the prevention of mold and rope in bread and other bakery products. Propionates have also been employed for preventing the growth of mold in certain packaged cheese. While acetic acid is not effective against mold, it can be used to reduce rope infection. *Sodium diacetate*,  $CH_3COONa \cdot CH_3COOH$ , has both a mold- and rope-preventive action. Butyric and valeric acids are good mold inhibitors but their odor prevents greater utilization.

**Glycols** (*q.v.*). *Propylene glycol*,  $CH_3CHOHCH_2OH$ , is better than glycerol and equal to ethyl alcohol as a mold inhibitor, but substantial amounts must be used. It has low *in vitro* germicidal activity, but it can be used as a germicidal mist because in

the form of an aerosol it can sterilize air. *Triethylene glycol*,  $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ , has also been proposed and used as an aerosol disinfectant. Ethylene glycol, diethylene glycol, and related compounds are not acceptable as food components because of their relative toxicity.

**Volatile Food Preservatives.** *Ethylene oxide* (q.v.), *propylene oxide*, and *methyl bromide*, all of which are highly volatile at room temperature, have been suggested as preservatives. Measured amounts of mixtures of these substances with a diluent such as water, alcohol, or propylene glycol are introduced by means of blotting paper or as a snow, prepared by freezing a mixture of the preservative and the diluent at  $-30$  to  $-70^\circ\text{C}$ ., into the container of the food immediately before sealing. The container must be permeable to the preservative. When stored at room temperature after sealing, the preservative evaporates, sterilizes the contents, and then escapes through the walls of the container, leaving virtually no trace of the agent. It is to be noted that these substances are fumigants and toxic.

**Other Organic Preservatives.** Many other substances have been proposed as preservatives for food. Some of these like formaldehyde, formic acid, salicylic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, chloropicrin, and hexamethylenetetramine are forbidden because of their toxicity, and their use is considered an adulteration. The *quaternary ammonium compounds*, such as the alkylbenzyltrimethylammonium chlorides and a host of others, have been proposed as food preservatives, but many of them are considered toxic and hence are prohibited for use in foods. Certain pyridinium derivatives are effective in preventing mold growth in storage. For example, egg washes for 3–5 minutes in 0.05% solutions of lauric and myristic esters of methylpyridinium derivatives,  $\text{CH}_3\text{C}_6\text{H}_4\text{NRX}$ , considerably reduce the bacterial count on the shell. *Chloroform* has been used in sodium chloride brine for the preservation of fish. It has the advantage that it evaporates on standing.

**Sulfur Dioxide and Sulfites.** Except for common salt (see p. 809) and the nitrates and nitrites, the main inorganic preservatives used in the processing of foods are sulfur dioxide and sulfites. These are widely used for the sulfuring of fruits and vegetables before dehydration and for the partial sterilization of grape must for the production of wine. Sulfur dioxide is one of the oldest antiseptics used for foods.

As has been mentioned, undissociated sulfurous acid is an efficient antiseptic only in relatively strongly acid solution, and the effectiveness of sulfur dioxide and sulfites, such as potassium or sodium metabisulfite,  $\text{K}_2\text{S}_2\text{O}_5$  or  $\text{Na}_2\text{S}_2\text{O}_5$ , depends on the amount of free sulfurous acid present. Substances such as glucose, which combine with sulfurous acid, reduce its action. Sulfur dioxide and sulfites are more effective against molds than against yeasts. They also have a retarding effect on enzymes.

**Oxidizing Agents.** Chemicals such as potassium bromate, potassium iodate, ammonium and potassium persulfates, calcium peroxide and other peroxides, and sodium chloride are often incorporated with yeast, or with yeast improvers or flour, to activate the yeast. They probably act as oxidative inhibitors of wheat proteinase but they also kill microorganisms. The amount of oxidizing agent used should not exceed 0.0075 part by weight for each 100 parts of flour by weight. See also "Maturation agents" and "Bleaching agents," pp. 845, 846.

Hydrogen peroxide has been utilized as a preservative for milk (not permitted by law), milk products such as cheese, and in pickles. One advantage claimed for it is its relative harmlessness and its conversion to water on decomposition. It has also been used in an antiseptic ice for the preservation of fish in transit and in brine solution in

the production of fish fillets (see *Fish*). Its preservative action under these circumstances was transient. Hydrogen peroxide is not decomposed rapidly in acid solution when its decomposition is not catalyzed. Consequently, under these conditions it maintains its preservative action for considerable lengths of time.

Sodium nitrite has also been used in antiseptic ices. Sodium nitrite is very soluble in water, and hence it is not feasible to use a eutectic ice with this chemical as is the case with benzoic acid. However, by preventing aeration during the freezing and drainage of the core, a variable proportion of nitrite can be occluded in all parts of the ice block. By crushing the block, a relatively uniform concentration of ice and nitrite can be obtained.

Sodium hypochlorite solution is used as a wash for apples and other fruits in order to prevent mold growth. Sodium hypochlorite and other compounds, principally organic, capable of releasing chlorine have been added to ice used for the icing of fish in transit.

**Other Inorganic Preservatives.** Many years ago fluorides, fluosilicates, fluoroborates, borates, and boric acid were used as food preservatives. These substances are now considered adulterants.

**Antibiotics (*q.v.*).** In view of the great expansion in the production of antibiotics such as penicillin (*q.v.*), streptomycin (*q.v.*), aureomycin, terramycin, and chloromycetin (*q.v.*—chloramphenicol) since World War II, it is likely that as prices are reduced more and more and as more of these agents are synthesized, they will be employed as food preservatives. Some European preserving agents (mostly mold preparations), presumably acting on the basis of their antibiotic contents, have been on the market for some time, and the effectiveness of various pure antibiotics has also been demonstrated, especially in reducing the thermal treatment required for the preservation of some foods. At the present time there is still serious doubt concerning the desirability, from the public-health standpoint, of using antibiotic agents in the preservation of foods consumed regularly or in large quantities. However, pilot-plant-scale use of subtilin as a food preservative was reported in 1950.

**Smoking.** The principal purpose of smoking meat, fish, and their products is the preservation of the foodstuff; an additional purpose is the increase of flavor. It is the opinion of various authorities that greater preservative action results from the dehydrating effect of the heating than from the chemical preservatives in the smoke. The slow burning of hardwood sawdust such as hickory, juniper bush, maple, and birch produces a smoke containing formaldehyde, creosote, phenols, and pyroligneous acid. The heat of the process and these chemicals coagulate the external proteins, and the action of nitrites and nitrates, if present, is accelerated. The addition of smoke chemical flavors to the sawdust or directly to the product being smoked is undesirable since it reduces or eliminates the actual smoking step.

## Antioxidants

### ANTIOXIDANTS FOR OILY FOODS

A serious type of spoilage in foods containing oils or fats is the development of rancidity. Such foods range from edible oils and fats through foods containing substantial amounts of a fatty component like peanut butter and whole milk powder to foods containing relatively little fat or oil like coffee and crackers. Rancidity may arise because of oxidative, hydrolytic, or ketonic degradation, but it is generally due to

oxidation through the formation of peroxides at the double bonds of fat molecules with subsequent breakdown of these peroxides to form aldehydes, ketones, and acids of lower molecular weight.

The substances used to retard oxidation in foods may be classified into two principal groups: (1) antioxidants (*q.v.*), of which the greatest number have a hydroxyl group and in many cases are phenolic in nature; and (2) synergists, which are acids (the combined action of two or more substances to produce an effect greater than a simple additive function is termed *synergism*).

Among the antioxidants are the tocopherols and/or the oils of which they are components or from which they may be extracted; *n*-propyl gallate, ethyl gallate, and gallic acid; nordihydroguaiaretic acid; gum guaiac and analogous gum resins; and other compounds of a phenolic nature such as vanillyl alcohol, coniferyl alcohol, and catechol mono-*n*-dodecyl ether. Examples of compounds which have a hydroxyl group but are not phenols are L-ascorbic acid and D-isoascorbic acid and their esters such as palmitates and stearates.

Two of the principal acids used as synergists are citric acid and phosphoric acid; however, an entire group including oxalic, tartaric, maleic, malonic, malic, pyruvic, succinic, fumaric, and aconitic acids have been proposed. Gallic acid and caffeic acid are examples of both the phenolic type and the carboxylic acid type.

There are other materials having antioxidant action. For instance, lecithin and other phospholipides derived from soybean oil have been utilized for such purposes. It is likely that the cephalin portion has the inhibitory action and several patents have been granted for the use of portions of the cephalin molecule.

A number of other substances have been proposed and used as antioxidants: raw oat flour (Avenex), preparations from cereals, grains, milk solids, hexuronic and glucuronic acids, catalase, ethyl and other esters of tyrosine, sugar amines such as glucamine, hydroxamic acids,  $\beta$ , $\beta'$ -thiodipropionic and similar acids and their esters, substituted  $\beta$ -mercaptopropionic acids, butylated hydroxyanisole, and various other materials like tannins. Of the two groups of sulfur-containing acids, the most practical are believed to be *thiodipropionic acid* and its dilauryl and distearyl esters. The toxicology and antioxidant effectiveness of these particular materials have been under investigation for several years. In their Memo No. 110, March 1948, the Meat Inspection Division approved the use of thiodipropionic acid and the above esters in animal fats. At the present time, however, the use of thiodipropionates has been limited to experimental evaluations. They are not available on a commercial scale. Commercial *butylated hydroxyanisole* (BHA) consists chiefly of a mixture of 2- and 3-*tert*-butyl-4-hydroxyanisole (3- and 2-*tert*-butyl-4-methoxyphenol). This much used antioxidant for lard and other animal fats is noteworthy because its effect carries through into foods, such as bakery products, made with the treated fat. Permission for the use of butylated hydroxyanisole alone and in combination with other antioxidants and synergists has also been granted by the Meat Inspection Division (Memo No. 118, December 1948). A liquid mixture (designated AMIF-72 by the American Meat Institute Foundation), containing butylated hydroxyanisole, *n*-propyl gallate, and citric acid dissolved in propylene glycol, is now on the market.

**Tocopherols.** The tocopherols are potent antioxidants. They belong to the vitamin E group of vitamins (*q.v.*).  $\gamma$ -Tocopherol has the greatest antioxidant activity,  $\beta$ -tocopherol next, and  $\alpha$ -tocopherol the least, whereas the vitamin activity is in the reverse order. The Meat Inspection Division of the U.S. Department of Agricul-

ture has approved the use of tocopherols in rendered animal fats, but the concentration must not exceed 0.03% and it must be used as a 30% concentration in vegetable oils when added as an antioxidant to lard or rendered pork fat.

***n*-Propyl Gallate** (see *Gallic acid*). One of the materials permitted to be used in fats in concentrations not exceeding 0.01% is propyl gallate (Meat Inspection Division Memo No. 104, April 1947). It can be prepared in relatively pure state. It is very soluble in alcohol but is only sparingly soluble in fats. However, very little is required. It is a good antioxidant for lard but its inhibitory action is not carried over to any extent into crackers.

**Nordihydroguaiaretic acid** (4,4-(2,3-dimethyltetramethylene)dipyrocatechol, ND-GA),  $(\text{HO})_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_3(\text{OH})_2$ , which can be obtained from creosote bush, *Larrea divaricata*, is a potent antioxidant. Its action has been carried over from shortenings into baked goods. Citric acid displays good synergistic action in combination with it.

**Gum Guaiac** (see *Gums*). This gum resin has been shown to be an effective antioxidant for various fats, particularly lard, chicken grease, and oleo oil, and for fat-bearing foods like dehydrated pork. Because it is not very soluble in fats, it is necessary to incorporate the gum resin during the rendering step or to dissolve it in a solvent such as acetic acid, which is subsequently removed from the fat by evaporation during the deodorization step or by means of vacuum distillation. The antioxidant action of gum guaiac is carried over fairly well into crackers. Phosphoric acid has good synergistic action with gum guaiac.

#### ANTIOXIDANTS FOR FRUIT AND VEGETABLES

When fruits and vegetables are cut, diced, sliced, or bruised, they become brown. The prevention of this browning is a serious problem.

**Ascorbic Acid** (*q.v.*). One of the substances used to prevent enzymic browning of unprocessed and frozen cut fruit such as peaches is L-ascorbic acid. Related compounds such as D-isoscorbic acid and D-glucoscorbic acid will also inhibit discoloration. Ascorbic acid has been combined with citric acid for the same purpose. It has been added to salt solutions, sirups, and to dry sugar, and these combinations have been used as dips, sprays, and powders to control discoloration.

**Sulfur Dioxide.** A strong inhibiting action on the darkening of the natural color of apricots, peaches, pears, and apples is exerted by sulfur dioxide. Brine solutions containing sodium sulfite are also used for this purpose.

**Other Substances.** Dilute solutions of citric acid and hydrochloric acid have been used as dipping solutions for the prevention of browning of sliced peaches. Thiourea was suggested several years ago, but because it has an effect on thyroid activity, its use is prohibited by the Food & Drug Administration.

#### Acidulants

Acids are added to various food products for two principal purposes. These are for the preservation of the food by decreasing the pH and for flavor. Most bacteria do not live or reproduce in an acid medium, and hence acids prevent most bacterial spoilage. Acids are used in almost every food industry, for instance in soda pop, in the manufacture of cheese, in meat preservation, in the manufacture of jam and jelly and gelatin desserts, in the preparation of pickles, sauerkraut, and similar products, as a

doctor in the manufacture of candies, and for condimental purposes. Acids or acid salts are also used in bakery products and baking powders for leavening, in artichokes and other products so that they can be processed at lower temperatures, and in asparagus and other vegetables for the prevention of darkening during processing.

The chief acids used are acetic acid and vinegar, citric acid, tartaric acid, and lactic acid. Phosphoric acid has had some use in beverages. During World War II, some attempts were made to use adipic, saccharic, and hydroxyacetic (glycolic) acids. Malic acid has also been used. A number of acid salts such as monocalcium phosphate, alum, and potassium acid tartrate or cream of tartar should be mentioned in this connection.

### Neutralizers and Ionic Adjusters

Neutralizers are common food chemicals but because of the stigma often associated with their use, particularly in dairy products (*q.v.*), they are often given less meaningful names. Thus the term standardization is employed to describe the use of neutralizers in the neutralization of sour cream for the manufacture of butter. Actually, the sour cream is not completely neutralized, for the concentration of the acid is reduced by the addition of such materials to about 0.1–0.3%. The object of adding neutralizers is to improve the keeping quality of the butter made from cream of high acidity. They also assist in reducing fat loss during churning and prevent undesirable flavors. *Lime* neutralizers are among the most important in buttermaking. They are placed in three groups: low-magnesium limes contain 5% or less of magnesium, medium contain 30–35% magnesium, and high contain 40–45% magnesium. Among the soda-type neutralizers are *sodium bicarbonate*, *sodium carbonate*, *sodium sesquicarbonate* ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ), and *sodium hydroxide plus sodium carbonate*. Combinations of neutralizers are generally used, in order to avoid an undesirable effect on the taste of the butter produced.

The use of neutralizers for the standardization of fluid milk and cream is not looked upon with favor. The purpose of the addition is to prevent the acidity from rising high enough to curdle the milk or milk product. In establishing the definitions and standards of identity for evaporated milk, the Food & Drug Administration banned the use of sodium bicarbonate because, while this salt could be used for stabilizing the milk, it might also be added for the purpose of neutralizing sourness to permit the use of unfit milk. In order to overcome the production of lumpy, grainy, or excessively thick, evaporated milk, the addition of *disodium phosphate*, *sodium citrate*, or both, or *calcium chloride* not exceeding 0.1% by weight of the finished evaporated milk, is permitted. *Calcium "lactophosphate,"* which is a mixture of calcium lactate, calcium acid lactate, and calcium biphosphate,  $\text{CaH}_4(\text{PO}_4)_2$ , has been proposed as a neutralizer in milk products.

*Lime* is employed in the neutralization of sugar-cane juice and sugar-beet extract for clarification (see Vol. 3, p. 907; *Sugar manufacture*). Alkalized chocolate or cocoa is prepared with the aid of sodium or potassium bicarbonate, carbonate, or hydroxide, magnesium carbonate or oxide, or any combination of these substances.

*Sodium alginate*, *sodium caseinate*, the *pectates* of strong bases, and, in general, salts of weak acids and strong bases have the ability to function as neutralizers in food products.

**Salt-Balance Adjusters.** The retention of greenness by chlorophyll and its de-



rivatives is directly related to the retention of pigment magnesium. Hence, the establishment of an alkaline environment is the means most commonly available for the preservation of the natural green color of vegetables. Various processes of adjusting the salt balance have been tried using calcium hydroxide, disodium hydrogen phosphate and sodium carbonate or magnesium hydroxide, and sodium carbonate and sodium phosphate. In one process, peas for canning are pretreated by immersion in 2% sodium carbonate solution for 30–60 minutes at room temperature; they are then blanched in 0.04% calcium hydroxide solution, and are finally processed in a salt-sugar brine containing a suspension of 0.1% of magnesium hydroxide.

The copper present in the hemocyanin of crab's blood can be stabilized by dipping in a brine containing lactic acid and small amounts of zinc or aluminum salts. This enables Atlantic crab meat to be processed without subsequent darkening attributable to copper sulfide formation.

**Ion Exchange.** The properties of some liquid foods can be altered by an exchange of cations. For instance, the removal of a portion of the calcium content of milk by passage through a zeolite exchanger yields a soft-curd milk. Calcium can also be removed from apple juice by an analogous method, leaving sodium malate in its place. Maple sirup can be deleaded by such processes.

### Firming Agents

Fruits and vegetables like fresh tomatoes contain pectic components, which are relatively insoluble. They form a firm gel around the fibrous tissue of the fruit or vegetable and prevent its collapse. In the case of canned tomatoes and other products, the addition of calcium salts causes the formation of a calcium pectate gel, which supports the tissues and affords protection against softening. Anhydrous calcium chloride (0.07%), calcium sulfate, and some other calcium salts are permitted for use in firming canned tomatoes, but the chloride and sulfate are by far the most important. They are also applied in a mixture with table salt in the form of tablets. Excessive amounts of calcium chloride give the tomatoes a salty or bitter taste and render the fruit tough or rubbery in texture.

Calcium salts, including calcium chloride (1%), are also used with raspberries and other berries for canning. For canned and frozen sliced apples, calcium lactate seems to be more desirable than the chloride, but both are permitted.

Potassium aluminum sulfate (alum) is sometimes used as a firming agent in the processing of pickles. The alum, however, acts as an astringent and gives pickles treated with it a tart taste (see also p. 810).

### Emulsifiers and Stabilizers

Emulsifiers and stabilizers may be placed in several groups, namely, those that stabilize, or aid in forming: (1) emulsions, (2) suspensions, (3) processed cheese, (4) jellies and jams, (5) foams, (6) the texture of frozen products such as ice cream and other frozen desserts.

**Emulsions.** Many emulsions are dispersions of an oily material in water or an aqueous solution (see Vol. 5, p. 712). Substances used to retard the rate at which oil globules coalesce fall into three groups: (1) those that equalize the specific gravity of the two phases; (2) those that increase the viscosity, such as the "true" (water-soluble) gums acacia, tragacanth, agar, karaya, locust kernel, and Irish moss; and (3) those

that consist of long-chain molecules with a hydrophilic group at one end and a hydrophobic group at the other. The substances in the third group and some of those of group two are called emulsifiers. These concentrate in the interface in oil-in-water emulsions and lower the interfacial tension. Fresh egg yolk, lecithin (*q.v.*), phospholipides, gelatin (*q.v.*), and a host of synthetic emulsifiers are in this category.

*Cellulose Ethers.* Among the synthetic and semisynthetic emulsifiers and stabilizers are the cellulose ethers, principally methyl cellulose sold in different viscosities under trade names such as Methocel, methyl cellulose (Hercules), and Tylose, and sodium carboxymethyl cellulose commonly called sodium cellulose glycolate and sold under such trade names as CMC, Carboxymethocel-S, Cellofas WFZ, and Fondin. Methyl cellulose is a cold-water-dispersible material and will not disperse in hot water or in concentrated alcohol solutions; it has no food value and is nontoxic. Sodium cellulose glycolate may find greater use in food because of its ease of incorporation.

*Mono- and Diglycerides of Fatty Acids.* The mono- and diglycerides of fatty acids such as oleic, palmitic, and stearic have been used in foods like margarine to prevent leakage or exudation of water (see *Glycerol*). *Sodium monostearin sulfoacetate*,  $C_{17}H_{35}COOCH_2CHOHCH_2OOCCH_2SO_2ONa$ , in combination with mono- and diglycerides, is used to help emulsification, minimize water leakage, prevent spattering, and improve the texture and pan-frying properties of margarines (*q.v.*). The use of the latter in "high-ratio" or "superglycerinated" shortenings permits the ratio of sugar to flour to be increased for bakery products. The various commercial glycerol stearates, oleates, and laurates are in reality mixtures of the principal monoglyceride with some of the diglyceride and some free glycerol. They are sold under many trade names, and one product known as *glyceryl monococate* is the edible monoester of the fatty acids of coconut oil.

*Propylene Glycol Alkylates.* Propylene glycol stearate, laurate, and monococate are another group of emulsifying and thickening agents.

*Mannitan Alkylates.* Mixtures of the various anhydrides of the hexitol mannitol, known as hexitans and hexides depending upon the degree of anhydridization and ring structure, form esters with the fatty acids, which can be used as emulsifying agents (see also *Alcohols, higher polyhydric*). The principal ones available are mannitan monostearate, monopalmitate, and monolaurate.

*Sorbitan Alkylates.* Analogous esters of the hexitans and hexides of sorbitol have also been prepared commercially, namely sorbitan monostearate, monooleate, monopalmitate, and monolaurate. A group of these agents are known under the trade mark Spans. Some of these are water-in-oil emulsifiers.

*Polyoxyalkylene Sorbitan Alkylates.* A series of polyoxyalkylene derivatives of the sorbitan alkylates, which are generally soluble in water and insoluble in vegetable oils, are known commercially as Tweens.

*Other Polyhydroxy Alkylates.* A group of higher acyl derivatives of polyhydroxy alcohols and of polyhydroxy ethers, some of which are said to be edible, are known as Emcols. They are hydrophilic colloids and are suggested for use as emulsifiers, spreaders, and dispersers. A series of polyoxyethylene alkylates have been prepared, which are nonionic surface-active agents. These are sold under the trade mark Myrj. In the 1950 tentative Federal definitions for bread, the polyoxyalkylene polyhydroxy alkylates and the polyoxyethylene alkylates were not included as optional ingredients.

**Suspensions.** Prevention or retardation of the precipitation of materials in sus-

pension is another function of stabilizers. The stabilization of fruit and vegetable juices may be taken as representative of this group. Products such as grapefruit juice, orange juice, and tomato juice contain pectins, which have a stabilizing effect in that they retard the settling of the colloiddally dispersed particles. More pectin is sometimes added to commercial fruit juices to increase their stability. In many instances, the food product itself contains an enzyme that may destroy the stabilizing power of pectins. For example, tomato juice contains pectin methoxylase (pectase), capable of splitting off methanol and leaving pectic acid, which does not have the colloidal properties of pectin. Inactivation of the pectase assists in stabilization, and additional stability is given by homogenization. Calcium salts (see p. 841) are considered stabilizers by some.

While chocolate and chocolate milk drinks contain naturally occurring substances derived from the cocoa ingredient, which assist in the retardation of fat separation and the settling of solids, often such materials as Irish moss extract, tapioca flour, and sodium alginate are added to assist in the stabilization of the drink.

**Processed Cheese.** Stabilizers are added to processed cheese to assist in the production of a homogeneous mass with a desirable texture (see Vol. 4, p. 815). The agents used are commonly termed emulsifiers, although most of them do not belong to the group described above. They are also known as plasticizers. The agents more commonly employed such as *sodium citrate*, *potassium tartrate*, *disodium phosphate*, and *sodium caseinate*, are alkaline in reaction. Since a proper pH is necessary for a good product, the acid ortho-, meta-, and polyphosphates, dibasic citric acid, or citric acid itself are added for adjustment. These substances are generally used on the basis of 1 or 2% by weight of the bulk cheese. *Calcium lactate*, another plasticizer, is considered to be better than sodium or potassium lactate.

**Jellies and Jams.** Pectin is a necessary component in ordinary jams and jellies, but it is well to note that a proper concentration of sugar and acid is necessary for an adequate product. Some fruits, like apples, contain sufficient pectin for jelly formation, whereas others, like strawberries, are generally deficient in pectin and it is necessary to add some.

**Pectins.** The pectins of commerce are of two major types, slow-setting and quick-setting. Quick-setting low-ester (low-methoxyl) pectins are produced from pectins by partial deesterification. While at least 50% sugar in the final product is needed for jelly formation with slow-setting pectins, low-ester pectins will form gels or jellies at much lower sugar concentrations, or even in the absence of sugar, if a trace of calcium is present (see *Pectic substances*).

Gelatin desserts may also be considered to be in this class since the gelatin sets to a jellylike product (see *Gelatin*).

**Foams.** Whipped cream, baked goods, and candy are among the food products in which foams are stabilized. In beer and other alcoholic beverages of that type and in nonalcoholic beverages like root beer, foam stabilization is important. Aerated products like whipped butter, aerated chocolate, and ice cream and other frozen desserts are also in this category. Surface-active agents such as long-chain organic acids and their salts and esters, some sugars, and alcohols readily form foams.

Cream with a fat content of over 30% contains components that assist in the formation of a relatively stable foam with air, but the stability and volume of foam produced can be greatly increased by use of nitrous oxide or carbon dioxide gas. In aerated chocolate and in whipped butter, naturally occurring ingredients serve to en-

trap the air. In the manufacture of ice cream, materials are added to increase the volume by means of air entrapment as noted below. In bakery goods, eggs are a principal foam stabilizer, although synthetic surface-active agents are being utilized for this purpose in increasing amounts. In confectionery, gelatin, albumen, and pectin are used.

**Frozen Desserts.** In ice cream (*q.v.*) and other frozen desserts, the smaller ice crystals tend to disappear and the larger crystals tend to grow larger as a result of alternate thawing and freezing while in storage and during transportation because of fluctuation in temperature. Stabilizers such as *gelatin* and *sodium alginate* are used to maintain an even texture, to prevent shrinkage, and to assist in the incorporation and retention of air. Because agitation affects the action of certain stabilizers, ice cream made at home has different requirements for stabilization. For this purpose, agar in combination with dried skim-milk powder is better than egg yolk, Indian gum, pectin, and gelatin. Agar or gelatin combined with mayonnaise is satisfactory for frozen fruit salads. Eggs are required for custard and French-type ice cream.

### Humectants

Humectants are hygroscopic materials, which prevent loss of moisture when they are incorporated into foodstuffs. The principal substances used for this purpose are glycerol, propylene glycol, sorbitol (see Vol. 1, p. 324), apple sirup, and invert sugar. Since these substances have different effects when used as humectants, mixtures may have more favorable properties than a single agent. *Arabinose* has been claimed to have humectant properties; whether gums like *acacia*, *cherry gum*, and *tragacanth* owe their humectant properties to the *arabinose* formed on hydrolysis, or to their colloidal properties, is a matter of dispute. Pectins also act as humectants.

### Maturation Agents

Certain fruits like citrus fruits, bananas, and tomatoes may remain a greenish color even though they are ripe from the point of view of taste and chemical characteristics such as sugar-acid ratios. In such instances *ethylene* is used to destroy the chlorophyll, which masks the ripe color of the foodstuff. This is termed "artificial ripening" or "artificial coloring." Melons, apples, pears, pineapples, and tropical fruits are also treated by this process, and celery is "blanched" by use of this gas. Acetylene has also been used for this purpose.

A more recent development has been the suggested use of *2,4-dichlorophenoxyacetic acid*, and some of its salts, esters, and other derivatives such as *2,4,5-trichlorophenoxyacetic acid*, which are plant-growth substances (*q.v.*) and potent herbicides. When very dilute solutions are sprayed on bananas and tomatoes, they serve to degreen the fruit and produce a "normal" color.

Unbleached freshly milled flour slowly improves in color and baking qualities on storage. With the aid of such materials as chlorine and nitrosyl chloride, this maturation process may be rapidly increased. Nitrogen trichloride used to be employed for this purpose but its use was prohibited by FD&C, SRA 2 rev. because rations containing flour in which this chemical was used caused epileptiform seizures in dogs.

Many chemicals are used for the rapid maturation or aging of alcoholic beverages such as whiskey and wine.

### Bleaching Agents

The principal oxidizing agents used for bleaching flour to improve the color are chlorine, nitrosyl chloride, nitrogen "peroxide" (dioxide), and benzoyl peroxide. The last two, in contrast to the chlorine compounds, have only a bleaching effect and no maturation effect on flour (see p. 837; also Vol. 3, pp. 619-24).

Sulfur dioxide is used for the bleaching of fruits and juices in addition to its preservative action, and hydrogen peroxide is also used as a bleach as well as a preservative. The gas maturation agents already considered may actually also be considered bleaching agents, for they bleach the undesirable chlorophyll color, giving the desirable color of the fruit or vegetable in question.

### Gas Storage

By lowering the oxygen content and increasing the carbon dioxide concentration, the respiration of fruits and vegetables can be controlled and thus these materials can be preserved by storage in artificial atmospheres. In the simplest method, the storage room is made airtight and only sufficient air is permitted to enter to maintain a known carbon dioxide-oxygen ratio. Other methods of control of the atmospheres are available.

Carbon dioxide has been used for the preservation of eggs (*q.v.*) by evacuating the air to less than 10 mm. Hg in the storage container and pumping in carbon dioxide until the pressure is somewhat greater than atmospheric. Inert gases such as nitrogen and carbon dioxide have also been employed for the storage of canned foodstuffs, such as evaporated milk, fruits and vegetables, and of Cheddar cheese. The loss of palatability of dehydrated foods when stored is reduced if inert atmospheres are used.

### Coatings and Wrappings

Coatings and wrappings are applied to foods for two principal purposes: first, to prevent the entrance of microorganisms, dirt, etc., and, second, to prevent the loss or access of water. Some coatings are applied as chemicals and thus are considered here (see also p. 813). An example is the coating of apples with sodium tetraborate or borax as a mold preventive. Oranges are sometimes coated with borax for protection against molds, and in addition are waxed and polished to prevent loss of moisture. Eggs and meat are sometimes preserved by dipping them into hot oil. The oil closes the pores in the eggshells and seals the cells of the meat. Eggs at one time were preserved by keeping them in lime water or by dipping them into a cream of slaked lime and water to form an impervious coating of calcium carbonate.

Metallic pectinates have been suggested as coatings for meat, candies, and other products. The coating is impervious to air and cannot be utilized by many bacteria and molds. Glycerol monostearate has been suggested as a protective coating for edible hygroscopic powders and the like. The product coated with this material does not absorb moisture or cake, yet still disperses readily when placed in water.

A thin film of natural or artificial wax on the surface of plant tissue is effective in reducing its rate of water loss and thus reduces wilting. However, waxing does not actually prevent the growth of bacteria or molds already present on the fruit or vegetable unless an antiseptic is incorporated with the wax.

Excellent control of orange decay has been claimed for short dips in aqueous

solutions of thioacetamide,  $\text{CH}_3\text{CSNH}_2$ , 8-hydroxyquinoline sulfate,  $(\text{HOC}_9\text{H}_6\text{N})_2\cdot\text{H}_2\text{SO}_4$ , and 2-aminothiazole,  $\text{NH}_2\text{C}:\text{N}:\text{CH}:\text{CH}:\text{S}$ .

**Impregnated Wrappers.** The use of wrappers impregnated with antiseptics is not novel and has been a common practice for years. A number of chemicals have been especially suggested for this purpose. For example, wrappers impregnated with sodium propionate and calcium propionate have been used to prevent mold growth on butter. Artificial and natural sausage casings have been treated chemically for the protection of the meat interior. Wrappers containing *o*-phenylphenol were effective in protecting oranges and lemons against microorganisms, and paper impregnated with formaldehyde has been used for the protection of butter.

**Mycostatic Vapors.** A variation of the use of chemicals in wrappings is the use of chemicals for the impregnation of such packings as the fillers and flats of egg crates. Such substances as sodium 2,4,5-trichlorophenate (Dowicide B) when used as indicated have sufficient vapor pressure to give off, slowly and continuously, a vapor with marked mycostatic action and thus prevent the growth of mold on eggs.

Bread can be packaged in paper containing 1-2% of a slowly vaporizing compound, such as dimethyl  $\alpha$ , $\beta$ -dichlorosuccinate,  $(\text{CH}_3\text{OOCCHCl})_2$ , crotonic acid,  $\text{CH}_3\text{CH}:\text{CHCOOH}$ , and derivatives of 2-hexenoic acid,  $\text{CH}_3(\text{CH}_2)_2\text{CH}:\text{CHCOOH}$ .

### Other Food Chemicals

There are many other chemicals used for functional purposes in food. Chief among these are the coal-tar and other colors and synthetic and other flavoring substances.

It will be illustrative of the expanded use of chemicals in the processing of foods to mention a few. In breadmaking, in addition to the yeast nutrients, improvers, baking powders, and flour bleaches and maturing agents already mentioned, the following compounds have been employed: calcium sulfate, calcium lactate, ammonium phosphate, ammonium sulfate, ammonium chloride, ammonium carbonate, ammonium lactate, and monocalcium phosphate.

A number of phosphates are commonly used. Disodium phosphate,  $\text{Na}_2\text{HPO}_4$ , and so-called sodium hexametaphosphate are used as emulsifiers in the manufacture of processed cheese. Disodium phosphate is also used in the adjustment of the acidity of evaporated or condensed milk. Tricalcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , is used as an anti-acid and as a conditioner to prevent the caking of sugar, salt, and other powdered materials. Disodium dihydrogen pyrophosphate (acid sodium pyrophosphate),  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ , is used as a leavening agent.

Calcium and magnesium carbonate and starch are used as "drying" or "free-flowing" agents to be added to powders. Silica gel and quicklime have been used as drying agents in special compartments of food containers.

In a discussion of the use of chemicals in food, it is pertinent to mention the use of proteolytic enzymes such as papain, from papaya, and bromelin, from pineapple juice, in tenderizing meats; of pectinases in the clarification of fruit juices and wines; and of amylases in the liquefaction and saccharification of starches. Rennin is used in the manufacture of cheese and as a component of certain milk-setting desserts. Invertase is used for the inversion of cane and beet sirups and as a doctor in candy (see *Enzymes*).

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FOOD PRESERVATIVES. See *Food chemicals*.

## FORENSIC CHEMISTRY

The field of forensic chemistry, more exactly termed "chemical criminalistics," relates to the application of chemical knowledge and techniques to the study of physical evidence. So broad is the underlying chemistry and so numerous its tools and techniques, that some relation exists between it and most of the branches of criminal investigation. Most phases of criminalistics, for example, firearms investigation, hairs and fibers, vegetable and mineral residues, fingerprints, tool marks, and tracks and and traces, involve chemistry only incidentally. They are therefore excluded from extended treatment here, although some authors classify virtually any, if not all, aspects of criminal evidence investigation under the heading "forensic chemistry," just as others do under the title "forensic medicine" (1,3,5).

The microscope is one of the most important instruments of the criminalist, and only an occasional but very powerful tool for the chemist. Photography, so important to the criminalist, is a chemical process, but one largely absent from the chemist's repertory. So also are biochemical and toxicological methods, for example, testing and typing of blood, detection of poisons, and many similar specialties. The choice of subject matter is therefore relatively arbitrary, as indeed is true of all published work in this important and expanding field.

The chief problems of the criminalist may be summarized as (1) determining the nature of a material, that is, identifying it; and (2) determining whether two materials or objects are identical. As a corollary to the question of identity, the degree and significance of such an identity must be evaluated. There is, for example, a great difference between the significance of two identical fingerprints and that of identity of species of two pieces of wood. The latter may be valuable information, but it does not prove identity of source.

Quantitative analysis is of less value to the criminalist than qualitative analysis. Identification and comparison rarely require quantitative chemical treatment. In certain aspects of toxicology, and particularly in diagnosis of drunkenness, the quantitative approach is essential. Examination of burned evidence may require quantitative determination of the ash constituents as a means of determining the nature of the material burned. At infrequent intervals, quantitative analysis for groups or constitu-

ents of a relatively pure material may be necessary to identify it. See *Analytical chemistry*.

#### PHYSICAL PROPERTIES

If two materials or objects are identical, they will exhibit identical physical properties, such as (1) density; (2) refractive index; (3) melting point; (4) boiling point; (5) flash or ignition point; (6) hardness; (7) fluorescence; and (8) absorption of radiation, including visible, infrared, and ultraviolet light, and x-rays.

Density, refractive index, and fluorescence are by far the most valuable of the physical properties. The first two are capable of identifying the source of broken-glass fragments with a probability of at least 100:1 (7). Density distribution of soil constituents serves to identify the source of the soil with a very high probability (9). Hair, paint, crystalline materials, and numerous other substances found at times in evidence may be identified on the basis of their densities and refractive indexes.

Fluorescence under ultraviolet light is widely employed in identifying physiological-fluid stains, alteration and obliteration of writing, and in determining the nature of many miscellaneous materials (10). The fluorescence of most substances, while not specific, is at least characteristic. It serves to eliminate many alternative possibilities of the nature of a residue or object; it locates otherwise invisible materials, such as stains or erased writing; and it gives a preliminary indication of the nature of a material. It may also be used to determine the presence of differences in composition of similar-appearing materials, such as glass fragments.

Boiling, flash, and ignition points are useful chiefly in the study of materials used in incendiarism and investigation of fires. It is at times possible to recover from an arson scene enough unconsumed fuel to allow comparison of the physical properties with those of standard fuels suspected of being used. These properties, combined with melting point, refractive index, and density, are also useful in those occasional instances when pure materials must be identified.

The determination of hardness serves in the identification of mineral materials and gems, and especially in establishing identity of metal fragments. Its utility is more restricted than is true of some other physical properties, and the determination is not ordinarily very accurate.

Absorption of visible radiation (light) is the cause of color. It is therefore of primary importance whenever colors are compared or used for identification purposes, as in the examination of textile fibers, hairs, paint, wood fragments, and many similar items. It is also the property that allows the use of photography, and may be extended photographically to absorption of infrared or ultraviolet radiations. The reproduction of obliterated and erased inks and pigments, printing or writing on burned documents, and similar problems are often solved by use of these invisible radiations in combination with photography (6,10).

#### CHEMICAL MICROSCOPY AND POLARIZED LIGHT

Qualitative detection and identification of minute amounts of elements and radicals are dependably performed by means of crystal-forming reactions under microscopic observation. See *Microscopy, chemical*. The combination of a selected reagent with observation of the crystals formed, as elaborated by Chamot and Mason, is perhaps the most specific microdetection method known (11). It is also one of the most



sensitive. It may be applied to nearly all inorganic ions and radicals as well as to many organic materials. Stevenson has summarized the crystal reactions of most of the important alkaloids (18). The resulting sensitive and rapid tests are, in general, superior to the more common color tests ordinarily employed. Similar formation of characteristic crystals, which may be identified microscopically, is employed widely in the well-known Teichmann test for blood, the similar Takayama blood test, and the Florence (potassium triiodide) and Barberios (picric acid) tests for semen (3,26). The uses of simple chemical microscopy are both wide and varied throughout the entire field of criminalistics.

Chemical microscopic methods are effectively supplemented by employing polarized light with the polarizing microscope. It is possible thus to study the birefringence of a crystal, its optic sign or sign of elongation, its characteristics of extinction, its refractive indexes in different orientations, and its pleochroism. All of these are characteristic of the individual crystal species and together they constitute a most powerful tool for the positive identification of any crystalline material (12). The studies of Whitmore and Wood have shown this technique to be of the very greatest utility in identifying crystals of alkaloids and their derivatives (20,21). It can be employed for identification of many other kinds of poison and for an indefinite number of miscellaneous crystalline materials of criminalistic interest.

#### SPOT AND COLOR REACTIONS

Spot and color tests have a very broad application in chemical identification. They are often more sensitive than crystal-formation methods, but are ordinarily less specific. Their ease and rapidity of performance commend them particularly for many types of preliminary testing.

Spot tests, as summarized by Feigl, are applicable to the general field of chemical identification (13,14). They have for this reason an important place in chemical criminalistics because of the wide variety of chemical problems that are encountered. As an illustration, corrosive, poisonous, or noxious chemicals are frequently used in sabotage, and may be identified partially or wholly by means of spot tests. Materials detrimental to motors are sometimes added to gasoline. Chemicals are thrown on furniture or other personal property. Industrial contamination of water supply, air, and soil constitutes a field in which the sensitive spot test is invaluable.

Color tests for poisons constitute the largest single application of this type of test. Few poisons exist for which color tests are not available (15,16,19). The crystal tests for poisons are usually of greater specificity, but they are less widely employed.

In shooting cases, it is common to use color tests to determine the powder pattern, and therefore the approximate distance of the gun at the time of firing (1,2). Nitrite in the pattern residue may be used to diazotize sulfanilic acid, which is then coupled with naphthylamine,  $\alpha$ -naphthol, or other suitable reagent. Color tests for nitrate ion are performed by means of diphenylamine in sulfuric acid with production of a blue color.

A very important type of color test is the catalytic oxidative test for blood. There are several variations of the test utilizing benzidine, leucomalachite green, phenolphthalein, luminol (3-aminophthalhydrazide), and other materials (4,25-27). All these are subject to rapid oxidation by hydrogen peroxide when a trace of blood pigment is present to catalyze the reaction. The first three, on oxidation, yield strong colors, while luminol responds to the presence of the most minute amounts of blood pigment with a strong chemiluminescence. All of these tests serve to locate invisible

quantities of blood and to give presumptive proof of their identity. Properly combined, they can serve as virtual proof of the presence of blood because of the differences in quantity and type of interfering materials to which each may react.

Staining reactions might be considered as belonging with chemical color tests. They are used widely for distinguishing between various physiological materials, fibers, and other materials having a distinctive type of morphology. These tests are based certainly to some extent on chemical combinations of the stain with constituents of morphological significance. They also involve solubility, absorption, and unknown factors, which, along with the chemical nature of the materials distinguished, serve to prove their presence and indicate their distribution.

#### POISON DETECTION AND IDENTIFICATION

The detection and identification of poisons involves chemistry more clearly and extensively than does almost any other aspect of criminalistics. The subject is both specialized and at the same time diverse in the various approaches that are made to it. This follows from the facts that (1) many different types of materials are toxic in the human body and may be capable of producing death or serious injury; (2) the amount available for testing is usually small; and (3) the toxic agent is ordinarily contaminated by a complex mixture of tissue, body fluids, ingested food, and other interfering materials from which the poison must usually be separated.

Poisons are commonly classified on the primary basis of a technical separation (toxicological) scheme rather than by their chemical nature. That there is a considerable degree of parallelism between the toxicological and the chemical classifications follows from the fact that toxic agents of similar chemical nature tend to fall in the same separation groups. There are glaring exceptions to this regularity. Both chemical and toxicological methods of classification fail to agree even approximately with the pharmacological classification, which is based on the effects produced by the poison. For convenience, an arbitrary toxicological classification will be followed in this discussion.

**Metallic Poisons.** In this category are included compounds of the common heavy metals mercury, lead, bismuth, silver, copper, zinc, thallium, and of the elements arsenic, antimony, and selenium. Of these, mercury, arsenic, lead, and perhaps thallium are by far the most important in terms of their toxic action and of frequency of their occurrence. Thallium poisoning, while uncommon, is of great violence and increasing incidence.

There is no general method for separating this group from physiological material, but the Reinsch test (formation of a dark metallic film on a strip of copper, immersed in boiling hydrochloric acid containing the test substance) serves to give preliminary indication of the presence of arsenic, antimony, bismuth, mercury, or silver. The simplicity of the test and the fact that it requires no destructive digestion of the sample make it of unique value as a preliminary examination method.

Standard chemical analytical methods may be followed for the isolation and identification of all of this group of poisons (16). Because of the high incidence of arsenic, mercury, and lead in poisoning cases, the Gutzeit test for arsenic, and the dithizone (diphenylthiocarbazone) methods, which are useful for both lead and mercury as well as other heavy metals, are popular. Quantitative analysis is often required, particularly in arsenic poisoning, because of the common presence of subtoxic quantities of this element in food and drugs, and its presence in small quantities as a probably

normal constituent of the animal body. While the semiquantitative Gutzeit method is most commonly employed, better results are obtained with the arsenomolybdate colorimetric method following separation of the arsenic in a volatile form, such as the trichloride. Industrial lead poisoning is of sufficient incidence to make necessary the quantitative determination of this element in many suspected nonacute as well as acute poisonings. See *Lead poisoning*. The spectrograph is often employed for metallic-poison testing with dependable qualitative and semiquantitative results (2).

Complete examination of stomach contents, organs, blood, or other physiological material for metallic poisons may require the application of many types of qualitative and quantitative analyses, most of which are attended by destruction of the organic constituents of the sample. The toxicologist must then apply such tests to small portions only, and rely largely on microchemical color and microscopic reactions, particularly for his preliminary testing.

**Volatile Poisons.** In this group are included only a few gases and such volatile liquids as organic solvents, along with the organic solids chloral hydrate and phenol, and the inorganic element yellow phosphorus. By far the most significant volatile poison is ethyl alcohol, quantitative determination of which in physiological materials is routine in most police laboratories. Most important in criminal homicide is perhaps hydrocyanic acid, usually derived from its salts.

The common property of this group of poisons is their separability from the physiological material containing them by means of distillation (often with steam). Because the distillation does not destroy most of the possible remaining poisons in the sample, this group is often removed before the other groups are studied at all. The actual identification and/or determination of individuals of the group assumes many forms. Cyanide, if identified, may be accepted as the cause of death because of its very great toxicity and normal absence from the animal system. The identification may be made by color tests as ferric ferrocyanide, ferric thiocyanate, or reaction with benzidine-copper acetate paper, guaiac-copper sulfate paper, etc., or it may be made crystallographically. Alcohol, also, occupies a unique position because of its wide use and low toxicity. Only the quantitative analysis for alcohol has real toxicological significance (17).

An increasing number of deaths are caused by volatile solvents, such as ether, gasoline, various aldehydes and ketones, benzene, aniline, nitrobenzene, carbon disulfide, carbon tetrachloride, and the higher alcohols. The origin of many of these is industrial and most are accidental. A large field of industrial toxicology is in the making, at least partially on this account. No generalized treatment of testing methods may be cited, but perhaps the most effective treatment is isolation of the material and identification through determination of its physical constants.

By comparison with the above-mentioned toxic agents, such materials as phenol, chloral hydrate, or yellow phosphorus are of limited importance, although they are occasionally used in both murder and suicide, and lead infrequently to accidental death.

**Nonvolatile Organic Poisons.** In this group are included more chemical individuals than in any other. They may be divided approximately into: (1) the toxic bases, which include the great group of alkaloids, the ptomaines, and a number of synthetic drugs; and (2) the nonbasic organic poisons, which include the barbituric acid derivatives, the glycosides, some polyphenols, certain essential oils, and a variety of natural and synthetic compounds, mostly acidie in nature. Most important, by far, are the

narcotic alkaloids such as morphine and cocaine, along with some violently toxic alkaloids such as strychnine, and the barbiturates, which are widely employed in suicide and to a limited extent in murder or criminal drugging.

The isolation of this group of poisons from physiological interfering materials is usually performed by some variation of the classical Stas-Otto procedure, which is now over a century old (15). Briefly, this system depends on the fact that (1) nearly all poisons of this group are soluble in alcohol, which separates them from the main portion of the viscera, etc.; and (2) the free bases (or acids) are soluble in immiscible organic solvents, such as ether or chloroform, while their salts are insoluble, and thus are not extracted. The poison is first extracted from slightly acidic solution with alcohol, and the dried residue is further extracted with an immiscible solvent. Successive extractions from acidic and basic solution serve to remove the bases from basic solution and the acids from acid solution. Neutral fat-soluble materials, such as simple fats, mineral oil, and the like, are constant interfering materials because they are extracted from either acid or basic solution. They interfere by preventing crystallization of the extracted poison and by direct chemical interference with the various tests. It is frequently quite difficult to purify the poison sufficiently to allow easy testing.

More modern procedures of isolating poisons in this group are being developed gradually (16). Some of these utilize as a preliminary step: (1) deproteinization; (2) freezing out of fats; (3) dehydration of the solution before extraction; and (4) other approaches. All of them resort to a final extraction, usually at controlled pH, in order to isolate the poison. Much cleaner separation may be achieved by resorting to some of these expedients as compared with the older Stas-Otto method and its common modifications.

Because only one of the poisons in a subgroup is normally present, further fractionation is rarely necessary. Spot or color tests may be applied to gain a preliminary notation of the nature of the poison separated. The results are then best confirmed by the more specific crystal tests, which can prove conclusively the identity of the poison tested. Absorption spectrophotometry is also useful for determination of some of this group.

A wide variety of reagents find application in testing, particularly for alkaloids, and to a lesser extent the other poisons of this group. Many of the reagents have been named after their originators. Thus, Wagner's reagent consists of nothing more than potassium triiodide solution; Sonnenschein's reagent is phosphomolybdic acid solution; Marme's reagent is potassium cadmium iodide solution; Frohde's reagent is ammonium molybdate in concentrated sulfuric acid; Mandelin's reagent is sodium vanadate in concentrated sulfuric acid; and Marquis' reagent is formaldehyde in concentrated sulfuric acid. Other reagents commonly used include strong oxidizing agents, such as potassium dichromate in sulfuric acid, and potassium permanganate in dilute sulfuric or nitric acid; and various heavy metal salts, such as gold and mercuric chlorides and copper sulfate. Chemical tests for barbiturates and most of the other synthetic drugs classified as poisons are less extensive and satisfactory than for alkaloids. For some of the drugs, particularly, and the poisonous glycosides, it may be necessary to resort to physiological testing with animals in order to ascertain the presence and nature of the poison.

**Gaseous Poisons.** Many gases are toxic and some of them are employed for criminal acts. Hydrogen cyanide is rarely encountered as such, but falls with the latile poisons, since it is most commonly taken in the form of one of its salts. Car-

bon monoxide is not to be classed with the volatile poisons because it is not distilled from the sample of poisoned blood but is tested in place, commonly by some variation of spectroscopic examination of blood, since carbon monoxide combines with the hemoglobin to form carboxyhemoglobin (carbonylhemoglobin), which exhibits a characteristic absorption spectrum. There are also a number of chemical tests that are of value. Hydrogen sulfide, chlorine, and phosgene are other common toxic gases for which chemical tests must occasionally be applied.

**Miscellaneous Poisons.** There are a wide variety of poisons that do not fall clearly in any of the above classifications and indeed are only infrequently encountered in toxicology. These include poisonous proteins, such as ricin from castor beans, a number of poisonous plants and fungi, and some plants containing narcotics, such as hemp, commonly termed marihuana. These require special chemical treatment, since they do not fit into the systematic procedures or classifications of the toxicologist. There exists also a large group of special industrial poisons, and various materials used at times in the cosmetic industry and as dyes for fur and hair.

#### CHEMICAL EXAMINATION OF DOCUMENTS

A number of the important problems of the document examiner may be solved through the use of chemical testing techniques. Virtually all of these are related to the chemical constitution of the writing material, the ink or pencil, etc., and at times the paper. The identity of the ink or other writing material, its obliteration or erasure, and its age are all problems in this category.

Even at the present time, one of the oldest types of ink, formed by combining an iron salt in acid solution with an extract of nut galls, is still the basis of the greater part of the ink used. Most of these inks contain also various dyes, while a number of modern inks are composed primarily of dye solution. Other inks are based on logwood extract and on carbon (lampblack) suspensions (22-24). See *Ink*. These general classes of inks are most easily distinguished experimentally by simple chemical tests, though microscopic observation alone is often effective. The combination of chemical and microscopic examination may be capable in most instances of determining the actual brand or manufacturer and type of ink, after making proper allowance for variations in age, ink density, and other factors. These tests are based usually on reactions for iron, the differential use of oxidizing or reducing agents that affect the dye color, and of acids and bases that alter some dye colors and may also markedly alter the appearance of the iron gallotannate.

Restoration of obliterations and erasures by chemical means is often possible through the application of simple chemical reactions. Ink that has been chemically bleached, as with ink eradicator, may often be restored with such reagents as ammonium sulfide or thiocyanic acid fumes, which react with the iron remaining in the paper. Fuming with iodine is at times effective also, but from selective adsorption on the paper fibers rather than from direct chemical reaction. To a limited extent, mechanical obliteration or erasure may also be restored by these means, but with more difficulty.

Under favorable circumstances, it is sometimes possible to estimate the age of old writing through study of changes that have occurred in the color of the iron gallotannate. Recent writing is subject to age estimation through examining the extent of diffusion of the chloride or sulfate ions from the ink line. Neither method is absolute or exact, and both must be applied with full realization of the importance of the physical

conditions of storage, the nature of the ink and paper, and the identity of factors affecting two documents being compared.

#### SPECIAL INSTRUMENTS

A number of special instruments are in use in the larger police laboratories. Among these, the spectrograph is pre-eminent in its application. See *Spectroscopy*. As mentioned above, the spectrograph has a number of useful applications where traces of certain elements, including a number of metals and some nonmetals, must be analyzed qualitatively and semiquantitatively. Its application in criminalistics is primarily to the study of those items of evidence in which the metallic content is of particular value in identification. These include metals and alloys as the most important single group. Here there is no chemical approach superior or equal to use of the spectrograph. Its application to paint identification is well known and widespread. When paint layers can be separated and studied individually, the spectrograph proves an extremely valuable tool. It has also been applied effectively to the identification of soils, glass, and various other similar items of evidence in which the metallic content, particularly, is of significance as a means of establishing identity.

The x-ray-diffraction camera has become of significance in the police laboratory in recent years, though its uses are still limited and it has not been widely adopted. X-ray diffraction is uniquely useful for identification of crystalline and pseudocrystalline materials (2).

The photoelectric spectrophotometer is likewise an instrument capable of wide application when quantitative analytical results are necessary (8). See *Colorimetry*. It is the ideal color-analyzing instrument and as such is applicable both to chemical analysis through production of color, as in determination of various toxic agents, and also to the study of ultraviolet absorption, which likewise is used for quantitative evaluation of materials that absorb in the ultraviolet regions, for example, barbiturates. It has an application as broad as the field of quantitative analysis itself as applied to criminal investigation.

Modifications of absorption spectrophotometry in other than the visible and ultraviolet ranges have not been widely employed. In this category is the infrared spectrograph. It is an instrument of the greatest value in the study of such materials as hydrocarbons and other organic materials whose chemical structure is in doubt, and it has been peculiarly valuable in petroleum-chemistry research. It may prove to be useful in arson investigation, but the applications are yet largely for the future.

The electron microscope, which is one of the more significant instrumental developments of recent times, appears not to have been directly applied to criminal investigation. It is not improbable that some such developments may occur in the future.

#### MISCELLANEOUS

The services of the chemist may be required in the analysis of ammunition to ascertain the manufacture or identity of the bullets or the propellant. Other common explosives, such as nitroglycerin, frequently require identification also. Again, the chemist may need to distinguish between the dyes on textiles, in inks, or on hair. The pigment of paint may require chemical identification, and tests for related materials, such as fingernail polish, lipstick, fuels, lubricants, and a host of miscellaneous materials, will at times engage the attention of the chemical criminalist.

For some of these problems, the emission spectrograph is most valuable. For others, the more conventional chemical and microscopic tests may be superior. The possible applications of chemistry in the field of physical evidence examination are so broad that complete coverage in a short treatment is impossible. It must suffice to state that almost every phase of criminalistics involves some chemical information, chemical technique, or at least the type of background and philosophy that can be considered characteristic of the properly trained chemist.

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P. L. KIRK

# FORMALDEHYDE

Formaldehyde (methanal (I.U.P.A.C.), oxomethane, methyl aldehyde),  $\text{HCHO}$ , formula weight 30.03, is the first member of the series of aliphatic aldehydes. Since pure formaldehyde is a gas at ordinary temperatures and cannot be readily isolated or handled in this state, it is marketed chiefly in the form of its aqueous solution (usually 37%  $\text{HCHO}$  by weight, N.F. IX., called mainly by the trade-marked names Formalin and Formol in Europe and in some industries in the U.S.) and the solid hydrated polymer paraformaldehyde ("paraform"),  $(\text{CH}_2\text{O})_n \cdot \text{H}_2\text{O}$ . The cyclic trimer *s*-trioxane ( $\alpha$ -trioxymethylene),  $\text{O} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2$ , is also manufactured on a limited scale. The tricyclic derivative hexamethylenetetramine (*q.v.*),  $(\text{CH}_2)_6\text{N}_4$ , produced by the reaction of formaldehyde with ammonia, is used commercially as a special form of formaldehyde.

Formaldehyde was first prepared by the Russian chemist A. M. Butlerov in 1859 as the product of an apparently unsuccessful attempt to synthesize methylene glycol by the hydrolysis of methylene diacetate. Although Butlerov failed to realize that he was dealing with formaldehyde, his description of its physical and chemical properties, including the isolation of paraformaldehyde, which he called dioxymethylene, and synthesis of hexamethylenetetramine are unquestionable. A. W. von Hofmann synthesized formaldehyde deliberately in 1868 by the reaction of methanol and air in the presence of a platinum catalyst and definitely established its chemical identity. Practical methods of manufacture developed with Loew's use of a copper catalyst around 1886 and Blank's silver-catalyst process patented in 1910. Commercial production was initiated in Germany in 1888, and manufacture in the U.S. commenced about 1901. However, production was on a limited scale before the commercial development of phenolic resins in 1910. In recent years, increasing quantities of formaldehyde are being manufactured by the oxidation of natural gas and the lower aliphatic hydrocarbons.

The major use of formaldehyde and its polymers is in the synthetic-resin industry, where it is employed principally in the production of thermosetting resins, oil-soluble resins, and adhesives by reaction with phenols, urea, and melamine. Under normal conditions, this use accounts for about 75% of the total production. Increasing quantities are consumed in making other chemicals such as hexamethylenetetramine and pentaerythritol, which consume about 10%. The remainder (about 15%) is used



in the manufacture of textiles, dyes, drugs, paper, leather, photographic materials, embalming agents, disinfectants, and insecticides, as well as in a large number of miscellaneous applications. As a result of wartime demands for hexamethylenetetramine and pentaerythritol for explosives, about 35% of the U.S. production was used for the manufacture of these chemicals in 1943-44 and only 50% for resins.

### Physical and Thermal Properties

#### ANHYDROUS FORMALDEHYDE

At ordinary temperatures, pure formaldehyde is a colorless gas possessing a strong pungent odor and extremely irritating to the mucous membranes of the eyes, nose, and throat. At low temperatures, it condenses to a clear, mobile liquid (f.p.  $-118^{\circ}\text{C}$ ., b.p.  $-19.2^{\circ}\text{C}$ .), which polymerizes to a solid reversible polymer, polyoxymethylene, on storage. On warming to room temperature in a sealed tube, it polymerizes rapidly with evolution of 15 kg.-cal. of heat per gram-mole. The completely anhydrous gas is relatively stable under atmospheric pressure at temperatures of  $80$ – $100^{\circ}\text{C}$ ., but it slowly polymerizes at lower temperatures. Polymerization is powerfully accelerated by traces of polar compounds such as acids, alkalies, and water. At temperatures of  $400^{\circ}\text{C}$ . and above, it decomposes chemically at appreciable rates to carbon monoxide and hydrogen.

Formaldehyde gas is combustible and forms explosive combinations with air in the range covering mixtures containing 7–73 vol. %. The autoignition temperature is reported as approximately  $300^{\circ}\text{C}$ . Thermodynamic properties of monomeric formaldehyde gas are: heat of combustion, 134.1 kg.-cal. per gram-mole (25); heat of formation at  $18^{\circ}\text{C}$ ., 28.3 kg.-cal. per gram-mole; free energy,  $-27.0$  kg.-cal. per gram-mole; heat capacity at 1 atm., 9.75 cal. per gram-mole at  $0^{\circ}\text{C}$ . and 10.49 cal. per gram-mole at  $100^{\circ}\text{C}$ . (calculated from spectroscopic data by the method of Dobratz). At ordinary temperatures, formaldehyde gas is readily soluble in water with which it reacts to form an equilibrium mixture of the dissolved monohydrate, methylene glycol (methanediol),  $\text{CH}_2(\text{OH})_2$ , and a series of low-molecular polymeric hydrates, polyoxymethylene glycols, having the type formula  $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ . Its heat of solution in water is 15 kg.-cal. per gram-mole. The gas is also readily soluble in alcohols, glycols, amides, and other polar solvents, which form solvates. The heat of solution in alcohols is approximately identical with the value for water. Formaldehyde is only slightly soluble in nonpolar solvents such as hydrocarbons, ethers, esters, and chlorinated products. In general, formaldehyde solvates are chemically reversible and the composition reacts as a solution of formaldehyde.

#### FORMALDEHYDE SOLUTION

The characteristics of aqueous formaldehyde are dependent upon the fact that it is both hydrated and polymerized in the dissolved state. Since it is usually handled as a solution, the composition and properties of the system formaldehyde-water are of special importance. Research studies have demonstrated that dissolved formaldehyde is essentially an equilibrium mixture as described above. However, ultraviolet absorption spectrums indicate that small concentrations of the unhydrated monomer are present under some conditions of temperature and concentration (3). The state of equilibrium depends on the concentration and temperature. At concentrations of 2% or less, the formaldehyde is practically all in the form of methylene glycol; at higher

concentrations, the solution contains increasing proportions of polymeric hydrates, the average degree of polymerization increasing with increasing concentrations of dissolved formaldehyde. An increase of temperature shifts the equilibrium in favor of methylene glycol and the lower polymeric hydrates. The rate at which equilibrium is attained after a change of temperature or concentration is slow at low temperatures, requiring over 2 days at 0°C. Polymers possessing a greater degree of polymerization than the trimeric hydrate,  $\text{HO}(\text{CH}_2\text{O})_3\text{H}$ , are only partially soluble at room temperature. This accounts for the fact that concentrated solutions (over 30%  $\text{HCHO}$ ) must be kept warm if solution is to be maintained. Alcohols, such as methanol, increase solution stability due to the formation of hemiacetals (for example,  $\text{CH}_2(\text{OH})-(\text{OCH}_3)$ ). The partial pressure of formaldehyde in equilibrium with the solution is low, due to solvation, and is a function of the methylene glycol concentration rather than the total formaldehyde content. Formaldehyde is apparently not appreciably associated in the gaseous state, and its partial pressure may be regarded as the decomposition pressure of the dissolved hydrate. These factors explain the fact that formaldehyde solutions may be concentrated by vacuum evaporation at low temperatures, whereas pressure distillation at high temperatures makes it possible to obtain concentrated distillates from dilute solutions. On distillation at ordinary pressures without rectification, the still residue is always somewhat more concentrated than the distilled solution. Fractional condensation of the vapors of boiling solutions results in increasing the ratio of formaldehyde to water in the uncondensed vapors, since water is the least volatile constituent of the mixed vapors.

Densities and refractive indexes of pure formaldehyde solutions are linear functions of concentration; they are given in Table I (13). The temperature coefficient for changes in density,  $\Delta d/\Delta t$ , in the range 15–30°C. is 0.0002 for a 15% solution and 0.0004 for a 47% solution (13).

TABLE I. Densities and Refractive Indexes of Pure Formaldehyde Solutions.

Concn. $\text{HCHO}$ , wt. %	$d_4^{18}$	$n_D^{18}$	Concn. $\text{HCHO}$ , wt. %	$d_4^{18}$	$n_D^{18}$
5.....	1.0141.....	1.3388	30.....	1.0910.....	1.3676
10.....	1.0299.....	1.3445	35.....	1.1066.....	1.3735
15.....	1.0449.....	1.3504	40.....	1.1220.....	1.3795
20.....	1.0600.....	1.3559	45.....	1.1382.....	1.3857
25.....	1.0757.....	1.3617	50.....	1.1570.....	1.3925

Methanol, which is often present as a solution stabilizer in commercial formaldehyde solutions, lowers its density and raises its refractive index as shown below for the normal 37% grade:

Concn. methanol, wt. %.....	0	5	10	15
$d_4^{18}$ .....	1.1128	1.1009	1.0890	1.0764
$n_D^{18}$ .....	1.3759	1.3766	1.3772	1.3778

Viscosities of formaldehyde solutions as measured with the Hoesppler viscosimeter (Du Pont laboratories) are given in Table II. Minimum temperatures requisite to prevent precipitation of polymers on long storage for various practical concentrations of formaldehyde and methanol are shown in Table III. However, since equilibrium changes in solution are slow, short exposures to lower temperatures than those shown in Table III will not lead to polymer precipitation. A 37% low-methanol solution

will remain clear for about 25 days at 80°F., and the 50% solution can be stored for 30 days at 131°F.

TABLE II. Viscosities of Formaldehyde Solutions.

Formaldehyde, wt. %	Methanol, wt. %	Temperature, °C. ( $\pm 0.1^\circ$ )	Absolute viscosity, centipoises
30	—	25	1.87
30	—	60	1.04
37	—	60	1.21
50	—	60	1.82
37	6	25	2.45
37	8	25	2.56
37	10	25	2.58
37	12	25	2.60

TABLE III. Minimum Storage Temperatures.

Formaldehyde, wt. %	Methanol, wt. %	Temperature	
		°C.	°F.
30	< 1	7	45
37	< 1	35	95
37	7	16	60
37	10	7	45
37	12	6	43
50	< 1	65	149

The freezing point of dilute formaldehyde solutions is lower than the freezing point of water and is proportional to the average molecular weight of the solute. Accurate data on strong solutions have not been obtained since polymer precipitation takes place before freezing.

Partial pressures of formaldehyde over aqueous solutions containing little or no methanol can be estimated by the empirical Lacy equation for 10–40% solutions at temperatures ranging from 20 to about 60°C.:

$$\log p_{\text{HCHO}} = 9.942 - 0.953(0.488)^{W/10} - 2905/T$$

where  $p_{\text{HCHO}}$  = partial pressure in millimeters,  $W$  = formaldehyde concentration in weight per cent, and  $T$  = absolute temperature. Methanol when present raises the partial pressure of formaldehyde. Partial pressure values for a 37% solution containing 1 and 9% methanol are 2.7 and 4.2 mm., respectively, at 35°C. Solutions containing up to 40% formaldehyde boil at about 100°C. Partial pressures for boiling solutions are (18):

HCHO, wt. %.....	3.95	8.00	12.1	20.1	25.9	30.8	35.7	42.0	49.8
$p_{\text{HCHO}}$ , mm. Hg.....	17.5	35.5	52.5	84.0	108.5	126.0	141.0	160.5	181.0

TABLE IV. Flash Points of Formaldehyde Solutions.

Formaldehyde, wt. %	Methanol, wt. %	Flash point	
		°C.	°F.
37.2	0.5	85	185
37.1	8.0	67	152
37.2	10.1	64	147
37.1	11.9	56	133

The flash point of formaldehyde solutions decreases with increasing formaldehyde and methanol concentrations. Data reported by the Underwriters' Laboratories for 37% solutions with the tag closed tester are given in Table IV.

In general, formaldehyde solutions are slightly acid and have pH values in the range 2.5–3.5. This acidity is due to traces of formic acid. Solutions in which the acid has been removed or neutralized gradually become acidic as a result of the Cannizzaro reaction.

#### FORMALDEHYDE POLYMERS

Formaldehyde polymers may be broadly classified as (1) linear and (2) cyclic polymers. The former include the polyoxymethylene glycols and their simple derivatives; the latter are represented solely by trioxane and the little-known cyclic tetraoxymethylene (20). The polyoxymethylene (*eu*-polyoxymethylene) produced by the polymerization of liquid monomeric formaldehyde is believed to be a linear polymer of high molecular weight. All of these polymers are reversible and can be employed as anhydrous or semianhydrous forms of formaldehyde.

The polyoxymethylene glycols are linear, hydrated polymers. Commercial paraformaldehyde is the outstanding member of this group. Polyoxymethylene glycol derivatives such as the dimethyl ethers and diacetates represent modified polymer types. Structures and properties of the various polymers described in the chemical literature are indicated in Table V (22).

**Paraformaldehyde** is a white solid having the characteristic irritating odor of formaldehyde. It is a mixture of polyoxymethylene glycols having the type formula  $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ , in which the value of  $n$  ranges from approximately 8 to 100. The above represents the accepted chemical definition of paraformaldehyde (21), and corresponds to a HCHO content ranging from 93 to 99%, the balance consisting of combined water. Commercial polymer types may contain from 91 to 98% HCHO. Paraformaldehyde or "paraform" is sometimes erroneously designated "trioxymethylene."

On heating, paraformaldehyde depolymerizes to yield a mixture of monomeric formaldehyde gas and water vapor. Its decomposition pressure at 25°C. is 1.45 mm. and at 58°C., 13.56 mm. (15). When warmed under pressure, it melts in the range 120–170°C. The actual melting range of an individual sample depends on the average degree of polymerization and distribution of polyoxymethylene glycols of various molecular weights. It dissolves in water with depolymerization and hydration to yield formaldehyde solution. It is also soluble in alcohols, phenols, and other polar solvents in which it can depolymerize to yield solvate systems. The rate of solution increases with temperature and decreases with increasing molecular weight. The pH of the solvent medium is extremely important. The rate at which paraformaldehyde dissolves in water reaches a minimum in the pH range 3–5, but increases rapidly at lower or higher pH values. Addition of alkaline or acidic materials also accelerates solution in nonaqueous solvents.

The heat of combustion of paraformaldehyde is reported as 122.1 kg.-cal. per  $\text{CH}_2\text{O}$  unit for a 94.6% polymer (26). Its heat of formation is approximately 41 kg.-cal. per  $\text{CH}_2\text{O}$  unit.

Paraformaldehyde reacts chemically as formaldehyde at a rate determined by the rate of depolymerization under conditions of use. Reactivity decreases with increasing molecular weight. On aging, the average molecular weight of a polymer sample tends to increase gradually with a consequent decrease in reactivity.

TABLE V. Formaldehyde Polymers.

Polymer	Type formula	Range of polymerization (approx.), %	CH <sub>2</sub> O content, wt. %	Melting range, °C.	Solubility <sup>a</sup>		
					Acetone	Water	Dilute alkali Dilute acid
<i>Linear<sup>b</sup></i>							
Polyoxymethylene glycols							
Lower polyoxymethylene glycols	HO(CH <sub>2</sub> O) <sub>n</sub> H	2-8	77-93	80-120	s.	v.s.	v.s.
Paraformaldehyde	HO(CH <sub>2</sub> O) <sub>n</sub> H	8-100	93-99	120-170	i.	d.s.	s.
Commercial paraformaldehyde	HO(CH <sub>2</sub> O) <sub>n</sub> H	8-50	95-97	120-160	i.	d.s.	s.
α-Polyoxymethylene	HO(CH <sub>2</sub> O) <sub>n</sub> H	> 100	99.0-99.9	170-180	i.	v.d.s.	s.
β-Polyoxymethylene	HO(CH <sub>2</sub> O) <sub>n</sub> H + trace H <sub>2</sub> SO <sub>4</sub>	> 100	98-99	165-170	i.	v.d.s.	d.s.
Polyoxymethylene glycol derivatives <sup>c</sup>							
Polyoxymethylene diacetates	CH <sub>3</sub> COO(CH <sub>2</sub> O) <sub>n</sub> COCH <sub>3</sub>	2-100	37-93	> 165	i. <sup>d</sup>	i.	d.s.
Lower polyoxymethylene dimethyl ethers	CH <sub>3</sub> O(CH <sub>2</sub> O) <sub>n</sub> CH <sub>3</sub>	< 100	72-93	> 175	—	i. <sup>e</sup>	d.s.
γ-Polyoxymethylene (higher polyoxymethylene dimethyl ethers)	CH <sub>3</sub> O(CH <sub>2</sub> O) <sub>n</sub> CH <sub>3</sub>	> 100	93-99	160-180	i.	i.	d.s.
δ-Polyoxymethylene	CH <sub>3</sub> O(CH <sub>2</sub> O) <sub>n</sub> CH <sub>2</sub> CH(OH)OCH <sub>3</sub>	> 100	96-97	150-170	i.	i.	d.s.
ε-Polyoxymethylene	(CH <sub>2</sub> O) <sub>n</sub> (?)	> 100 (?)	99.7-99.9	195-200	i.	i.	—
eu-Polyoxymethylene	(CH <sub>2</sub> O) <sub>n</sub>	5000 (approx.)	100	170-185	i.	i.	v.d.s.
<i>Cyclic<sup>f</sup></i>							
s-Trioxane (α-trioxymethylene)	(CH <sub>2</sub> O) <sub>3</sub>	3	100	61-62	s.	s.	s.
Tetraoxymethylene	(CH <sub>2</sub> O) <sub>4</sub>	4	100	112	s.	s.	s.

<sup>a</sup> s. = soluble, v.s. = very soluble, d.s. = difficultly soluble, i. = insoluble. In the case of linear polymers, solution in water is accompanied by hydrolytic decomposition, which is catalyzed by alkalis and acids. Solubility as ordinarily observed is a measure of this depolymerization process, since only the lower polyoxymethylene glycols are more than slightly soluble. Cyclic polymers dissolve as polymers and give true solutions.

<sup>b</sup> On vaporization, linear polymers depolymerize to monomeric formaldehyde gas.

<sup>c</sup> Derivatives of low molecular weight do not depolymerize on vaporization.

<sup>d</sup> For  $n > 10$ .

<sup>e</sup> For  $n > 15$ .

<sup>f</sup> On vaporization, cyclic polymers do not depolymerize.

Source: reference (22).

**s-Trioxane**,  $\text{O.CH}_2\text{O.CH}_2\text{O.CH}_2$ , is the stable, cyclic trimer of formaldehyde.

It is a colorless, crystalline solid; m.p.  $64^\circ\text{C}$ ., b.p.  $115^\circ\text{C}$ . It has a characteristic chloroformlike odor and forms rhombohedral needles which are tough but pliant. The density of the molten polymer is 1.17 at  $65^\circ\text{C}$ . It ignites and vaporizes readily, and air saturated with its vapors between  $38$  and  $78^\circ\text{C}$ . forms explosive mixtures. It is soluble in water, alcohols, ketones, phenols, and most organic solvents, but is only slightly soluble in pentane and the lower paraffins. Solubilities in water at  $18^\circ$  and  $25^\circ\text{C}$ . are 17.1 and 21.1 grams per 100 ml., respectively. The heat of combustion of trioxane is variously reported at  $118.9 \pm 0.3$  kg.-cal. and 109.5 kg.-cal. per  $\text{CH}_2\text{O}$  unit. Its heat of formation at  $18^\circ\text{C}$ . is approximately 43 kg.-cal. per  $\text{CH}_2\text{O}$  unit. Its heat of vaporization is calculated as 3.3 kg.-cal. per  $\text{CH}_2\text{O}$  unit.

Pure trioxane shows no appreciable depolymerization at temperatures below  $250^\circ\text{C}$ . in the absence of decomposition catalysts. In aqueous solution, it is slowly depolymerized by strong acids but is inert to alkalis. In nonaqueous systems, it is readily converted to monomeric formaldehyde by small concentrations of strong acids at a rate determined by the acid concentration (24). It can be employed as a controllable source of anhydrous formaldehyde in nonaqueous reactions.

### Reactions

Formaldehyde is extremely reactive and will combine chemically with practically every type of organic chemical with the exception of the paraffins (see also "Reactions" under *Aldehydes*). It can be employed in the form of anhydrous monomer, solution, or polymer with essentially equivalent results. In general, the form used is of importance chiefly in its effect on the rate of reaction. Monomeric and polymeric forms are of special value where the presence of water is undesirable. Solutions and polymers are less reactive than the monomer, since they represent lower energy potentials in which the aldehyde has already reacted with itself or water.

On reduction, formaldehyde is converted to methanol; oxidation gives formic acid or carbon dioxide and water. The Cannizzaro reaction in aqueous solution gives formic acid and methanol in equimolar proportions:

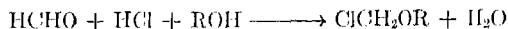


This reaction is accelerated by alkalis but also accounts for the gradual increase in the acidity of commercial solutions on long storage. Formaldehyde condenses with itself in an aldol-type condensation to yield the lower hydroxy aldehydes, hydroxy ketones, and hexose sugars. This reaction is apparently autocatalytic and is favored by alkaline conditions. The condensation, which is characterized by a long incubation period, appears to be most readily initiated by the presence of hydroxides of alkaline earths and weakly basic metals. Formaldehyde acts as a strong reducing agent in the presence of alkalis and can be employed to precipitate metals from solutions of gold, silver, copper, and mercury, and to reduce other carbonyl compounds to alcohols.

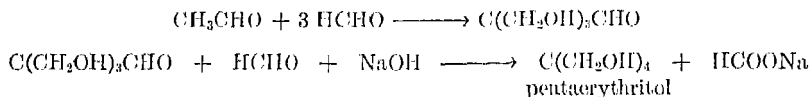
In general, the major chemical reactions of formaldehyde with other compounds involve the formation of methylol (hydroxymethyl),  $-\text{CH}_2\text{OH}$ , or methylene,  $=\text{CH}_2$ , derivatives. Polycondensations lead to the formation of high-molecular resins in which molecules of the other reactant are linked together by the methylene groups. Alkaline catalysts tend to favor the formation of methylol derivatives, whereas acids usually favor the production of methylene bridges. Methylol derivatives are probably

the primary reaction products, although, in many cases, they are extremely reactive and undergo condensation reactions to form methylene derivatives even under alkaline conditions.

With acidic catalysts, formaldehyde and alcohols, glycols, or polyhydroxy aliphatics (for example, sugar, cellulose, starch, and polyvinyl alcohol) react to give formals (methylene ethers),  $\text{CH}_2(\text{OR})_2$ , whereas unstable hemiacetals,  $\text{CH}_2(\text{OH})(\text{OR})$ , are produced under neutral or alkaline conditions. Formaldehyde reacts with hydrogen halides and alcohols to give  $\alpha$ -halomethyl ethers:

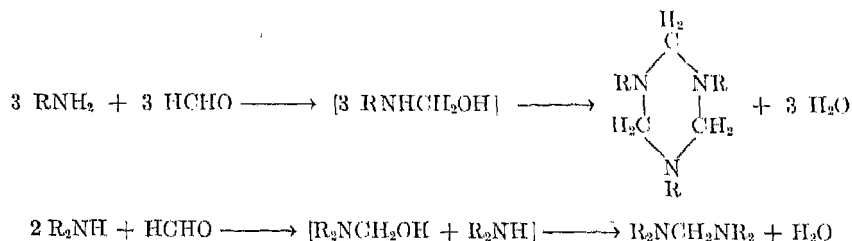


Mercaptans react like alcohols to give analogous thio derivatives. In the presence of alkalis, aldehydes and ketones containing  $\alpha$ -hydrogen atoms form mono- and polymethylol derivatives, which can be further reduced to give polyalcohols, as illustrated by the formation of pentaerythritol from acetaldehyde:

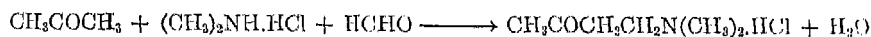


Other aliphatic compounds containing active hydrogen atoms also form methylol derivatives with alkaline catalysts. These include nitroalkanes, cyanoacetates, and malonic esters. Phenol and many substituted phenols form methylol compounds (phenol alcohols), which undergo polycondensation to give phenol-formaldehyde resins. The methylol groups enter the ortho and para positions on the benzene nucleus; if these positions are blocked, the ordinary nuclear condensations cannot take place. Acid catalysts lead to immediate polycondensation and do not, in general, permit isolation of the simple methylol derivatives, which is often possible when alkalis are employed.

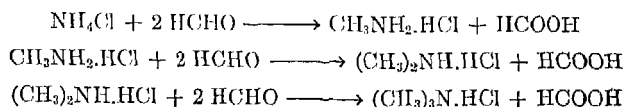
Ammonia and amines condense readily with formaldehyde to give simple or cyclic methylene derivatives. Formation of hexamethylenetetramine by the reaction of formaldehyde with ammonia is paralleled by the formation with primary amines of cyclic trialkyl or triaryl trimethylenetriamines (hexahydro-*s*-triazines), and with secondary amines of symmetrically tetrasubstituted methylenediamine (methanediamine). Tertiary amines do not react. Unstable methylol derivatives are apparently the primary products:



The well-known Mannich reaction involves the condensation of ammonia, a primary amine, or a secondary amine, usually in the form of a hydrochloride, with formaldehyde and a compound containing one or more active hydrogen atoms. The following reaction is typical:



When formaldehyde is heated with amines or ammonium salts under acid conditions, the primary products are reduced with the formation of methylamines:



Amides give relatively stable methylol derivatives under alkaline conditions. The methylolureas ((hydroxymethyl)ureas) undergo polycondensation, producing urea-formaldehyde resins. Melamine reacts in a manner similar to urea, yielding polymethylol derivatives and resins. Proteins are hardened and insolubilized by reaction with formaldehyde as a result of the formation of methylene cross linkages.

Organic and many inorganic acids react with formaldehyde to form methylol and methylene derivatives. Fatty acid anhydrides give both methylene and polyoxymethylene diesters. A polymeric methylene sulfate is obtained from paraformaldehyde and fuming sulfuric acid. With hydrochloric acid, the primary product, although not isolable, is probably chloromethanol,  $\text{ClCH}_2\text{OH}$ ; bis(chloromethyl) ether is readily obtained when a solution of paraform in cold sulfuric acid is saturated with hydrogen chloride:

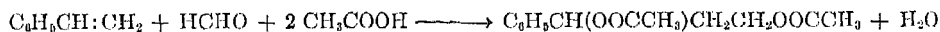


Hydrogen sulfide precipitates cyclic trithiane,  $\text{S}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CH}_2$ , from formaldehyde

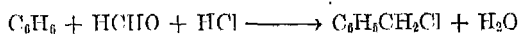
solution under strongly acidic conditions and, in the absence of acid catalysts, yields complex polymethylene derivatives, called formthionals (28). Hydrogen cyanide reacts readily to form formaldehyde cyanohydrin (glycolonitrile),  $\text{CH}_2(\text{OH})\text{CN}$ , in the presence of traces of alkali. Ketene reacts with formaldehyde to form the cyclic  $\beta$ -propiolactone (hydraacrylic acid  $\beta$ -lactone),  $\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2$  (16).

Aqueous formaldehyde and sodium bisulfite form sodium formaldehyde bisulfite, which has been shown to have the structure of a hydroxy sulfonic acid,  $\text{HOCH}_2\text{SO}_3\text{Na}$  (22). This compound is soluble in water and methanol, but only slightly soluble in ethyl alcohol. On reduction with zinc dust and acetic acid, it yields sodium formaldehyde sulfoxylate,  $\text{HOCH}_2\text{SO}_2\text{Na}$ , which can also be obtained by treating formaldehyde with sodium hydrosulfite,  $\text{Na}_2\text{S}_2\text{O}_4$ , in the presence of caustic soda. Zinc formaldehyde sulfoxylate can also be obtained. See *Sulfur compounds*.

Unsaturated and aromatic hydrocarbons react with formaldehyde in the presence of strong acids. The olefin reaction (*Prins reaction*) usually results in the formation of a 1,3-glycol or an unsaturated alcohol in the form of an ester or formal. For example, when styrene reacts with paraform in acetic acid containing some sulfuric acid, the product is the diacetate of 1-phenyl-1,3-propanediol:



Aromatic hydrocarbons yield simple methylene or polymethylene derivatives. Benzene gives rise to a mixture of diphenylmethane and a hydrocarbon resin, Formolite. The chloromethylation reaction, by which  $-\text{CH}_2\text{Cl}$  groups are introduced on the aromatic nuclei, is of outstanding synthetic importance. Chloromethylation takes place when hydrogen chloride is treated with a mixture of an aromatic hydrocarbon and formaldehyde solution, paraformaldehyde, or trioxane:





Heat and special catalysts such as zinc chloride are often required. This reaction takes place readily with phenolic ethers, amides, and many other compounds containing active hydrogen atoms.

Acetylene reacts with formaldehyde in the presence of copper acetylide to yield 2-butyne-1,4-diol,  $\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$ , and propargyl alcohol (2-propyn-1-ol),  $\text{CH}\equiv\text{C}-\text{CH}_2\text{OH}$  (*Reppé reaction*). Formaldehyde and hydrogen chloride react with acetylene to yield 5-dichloromethyl-1,3-dioxane,  $\text{O}.\text{CH}_2.\text{O}.\text{CH}_2.\text{CH}(\text{CHCl}_2).\text{CH}_2$  (37).

The reactions of heterocyclic compounds with formaldehyde are similar to those involving unsaturated hydrocarbons and aromatics. Thiophene,  $\text{S}.\text{CH}:\text{CH}:\text{CH}:\text{CH}$ , forms resins readily in the presence of acid catalysts and gives simple and complex Mannich bases with formaldehyde and amines. Similarly sylvan (2-methylfuran),  $\text{O}.\text{C}(\text{CH}_3):\text{CH}:\text{CH}:\text{CH}$ , also takes part in the Mannich synthesis, and pyrrole,  $\text{NH}.\text{CH}:\text{CH}:\text{CH}:\text{CH}$ , yields *N*-methylol and *C*-methylol derivatives. The reaction with  $\alpha$ -picoline (2-methylpyridine),  $\text{N}:\text{C}(\text{CH}_3).\text{CH}:\text{CH}:\text{CH}:\text{CH}$ , involves the side chain, with the formation of 2-(hydroxyethyl)pyridine, which on dehydration yields 2-vinylpyridine (11).

## Manufacture

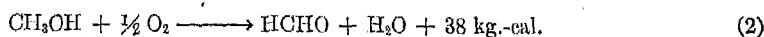
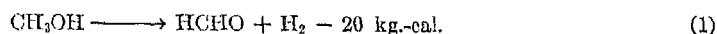
### FORMALDEHYDE SOLUTION

Formaldehyde solution is manufactured in large part from methanol, but increasing quantities (about 20% in 1948) are produced by the direct oxidation of natural gas and the lower petroleum hydrocarbons. The former procedure gives essentially pure formaldehyde containing some methanol and traces of formic acid as a primary product, whereas the latter gives a mixture of lower aliphatic aldehydes, alcohols, and acids, which on refining yields an extensive group of petrochemicals. Since methanol is synthesized from a carbon monoxide-hydrogen mixture produced from coal and water or from natural gas, hydrocarbons may be the fundamental raw material in either method of manufacture.

Other methods such as the hydrogenation of carbon monoxide and pyrolysis of formates have not led to industrial processes. The apparent simplicity of the carbon monoxide process is offset by a hopelessly unfavorable equilibrium even at high pressures.

**Methanol Processes** (9,17). These processes involve passing a mixture of methanol vapor and air over a stationary catalyst at approximately atmospheric pressure and absorbing the product gases in water. Two types of procedure are in use: one employs a silver or copper catalyst, operates with a rich methanol-air mixture, and yields a primary product solution containing unreacted methanol; the other employs an iron-molybdenum oxide catalyst, operates with a lean methanol-air mixture, and yields a substantially methanol-free product solution (14).

Formaldehyde is formed by two gas-phase reactions involving the dehydrogenation and oxidation of methanol:



These reactions may take place simultaneously in the metal-catalyzed process, although there is some evidence that this is solely a dehydrogenation reaction accompanied by combustion of a portion of the liberated hydrogen. The oxide process is primarily a true oxidation (see eq. 2).

Raw materials employed are chemically pure, synthetic methanol, air, and water. The air is filtered and may be washed, if necessary, to remove contaminants such as sulfur dioxide, which is stated to be injurious (17).

The first manufacturing step is the production of a methanol-air vapor mixture, which is fed to the catalytic converters. This is carried out either by flash vaporization of methanol, which is then mixed with air under controlled conditions, or by passing air through methanol maintained at the temperature requisite to obtain the desired mixtures. For safety, explosive mixtures of methanol and air must be avoided, and flame arrestors, explosion disks, etc., must be used wherever there is danger of accidental fires or explosions. The explosive limits for methanol-air mixtures are vari-ously reported, but are generally not broader than from 6 to 37% methanol by volume at 60°C. In this connection, it must be remembered that the range of flammability increases with increasing temperatures and is also influenced by pipe or reactor diameters. In the silver- or copper-catalyzed process, mixtures containing up to about 50 vol. % are normally employed.

The feed vapors, usually preheated, are passed into the converters or burners, which may consist of jacketed vessels containing a shallow bed of the prepared catalyst. The exact structure of the burner varies, but, in general, there is a plurality of converters, and provision is made for some cooling to prevent excessive reaction temperatures. The temperature for a silver-catalyst reactor is reported to vary from 450 to 650°C. with the optimum at about 635°C. (17). Product vapors are passed directly to a series of countercurrent scrubbers which cool the gases and dissolve the formaldehyde. The off-gases emerge from the tail scrubber. The scrubbers may take the form of packed or plate columns with the liquor cooled and recirculated. A trombone or spill cooler is usually employed. The primary product solution, which contains some methanol, must be adjusted to meet customer requirements with respect to its methanol and formaldehyde contents. Excess methanol is removed by fractionation, so that a substantially methanol-free solution can be obtained, if desired.

In the silver- or copper-catalyzed process, the dehydrogenation reaction and the oxidation of methanol or liberated hydrogen take place simultaneously at roughly equivalent rates, so that the off-gas contains 18–20% hydrogen and under 1% oxygen. Conversions ranging from 60 to 73% have been reported for the process with net yields of 83–92%. It has been stated that net yields from the oxide process are of the same order of magnitude, conversions being approximately equivalent to the theoretical yield. Improper control of these processes or dirty catalyst leads to formic acid production and low yields; inadequate cooling of the converter gases leads to production of methylal by reaction of formaldehyde and methanol (17).

In general, stainless steel is the preferred material for formaldehyde processing. Ordinary steel may be employed for the storage and handling of methanol, and aluminum may be used for scrubbers and formaldehyde storage. Recommended materials for storage of formaldehyde are 18–8 stainless steel, glass, stoneware, acid-resistant enamels, rubber, and aluminum. Phenolic-resin coatings and asphalt-based paints can also be used in the preparation of fairly resistant storage tanks. Iron, copper, nickel, and zinc alloys should be avoided.

**Hydrocarbon Processes.** These processes involve partial oxidation of a hydrocarbon gas with air or oxygen under pressure, followed by rapid cooling, condensation, and absorption of the products in water to give a crude solution, which must then be refined to separate formaldehyde from the other reaction products, such as methanol, acetaldehyde, propyl alcohol, propionaldehyde, and organic acids. Formaldehyde is isolated as a dilute solution, which must be concentrated to market strength. This solution is not the major product from these processes, the quantity and distribution of other products being dependent on the hydrocarbon raw material and processing technique. In one procedure it is reported that the major portion of the formaldehyde is obtained from the primary product methanol by the older process (5).

In general, the temperature at which aliphatic hydrocarbons oxidize at an appreciable rate is highest for those of small molecular weight. Methane, for example, usually requires a temperature of about 600°C. to initiate oxidation, whereas formaldehyde begins to decompose at an appreciable rate at 400°C. Higher hydrocarbons react at temperatures of 400–500°C. or below. This facilitates isolation of formaldehyde in practical yield. However, higher hydrocarbons yield increasing quantities of other than one-carbon products. High pressures increase alcohol formation, so that even gases containing a major portion of methane can be treated to give appreciable quantities of methanol with proper control. Partial oxidation of hydrocarbons can be accomplished with or without a catalyst, control being maintained by using an excess of hydrocarbon and promptly quenching the hot reaction gases to prevent decomposition reactions. In general, the conversion per pass is low, and the primary product solutions are relatively dilute.

Raw materials for hydrocarbon processes include natural gas or liquefied propane or butane, air or oxygen, and water.

In a typical procedure, liquid butane stored in a pressure tank is vaporized, preheated, and mixed with compressed air and steam at about 400°C. and 300–400 p.s.i. The reaction products are quenched with water and passed into a scrubber. Refining procedures may include fractionation, liquid–liquid extraction, azeotropic distillation, and extractive distillation. Exact processing details and reactor design have not been disclosed. A patent example discloses that 100 lb. butane can be converted to 15.2 lb. formaldehyde (100%), 19.6 lb. acetaldehyde, 7 lb. acetone, 19 lb. methanol, 1 lb. propyl alcohol, 0.5 lb. butyl alcohol, and 11.4 lb. organic acids. The yield of these products can be varied by control of pressures, temperatures, and feed ratios in the reaction step. Products manufactured by oxidation of propane and butane include formaldehyde, acetaldehyde, acetone, propionaldehyde, methanol, *n*-propyl alcohol, isopropyl alcohol, and butyl alcohols (4,8,30).

A natural-gas oxidation process employs mixed catalysts containing aluminum phosphate and metal oxides and pressures ranging from 100 to 300 p.s.i. with reaction temperatures around 450°C. Major products include formaldehyde, acetaldehyde, methanol, and methyl acetone (4,33). Another process is reported to oxidize natural gas, from which liquefiables have been removed, with 90–95% oxygen under pressure to produce methanol, acetaldehyde, and some formaldehyde. The gaseous products are passed through a conventional water scrubber giving a product solution which is separated into its constituents by fractionation leaving a residue consisting of an aqueous solution of salts of organic acids (5).

Materials of construction employed in these processes generally involve steel and stainless steel for equipment which is in contact with formaldehyde solution. Outdoor

refinery structure is characteristic, and the metal equipment is protected from weathering by aluminum paint.

#### PARAFORMALDEHYDE AND TRIOXANE

**Paraformaldehyde** is normally manufactured by the vacuum concentration of aqueous formaldehyde solution to the point where solidification of the polymer takes place. The process is usually controlled so that a product containing 91–98% formaldehyde or more is obtained. The vapors from this distillation process are condensed yielding dilute formaldehyde as a by-product. As in the manufacture of formaldehyde itself, stainless steel is the preferred material of construction.

**Trioxane** is produced by distilling concentrated (60% or greater) formaldehyde solution in the presence of a nonvolatile acid catalyst (for example 2% sulfuric acid). The crude-product distillate is a mixture of trioxane and aqueous formaldehyde, from which the trioxane may be isolated by extraction with a water-immiscible solvent such as methylene chloride (23). Crude trioxane can be purified by distillation at atmospheric pressure, since it boils without decomposition at approximately 115°C.

#### Production and Prices

Formaldehyde production has expanded almost without interruption since manufacture was first initiated. Along with the development of large-scale streamlined methods of manufacture the price has been consistently lowered. It has been estimated that the formaldehyde-production capacity of the U.S. is approaching a potential of approximately 1,000,000,000 lb. annually of 37% solution (27). Table VI gives U.S. production and approximate prices for formaldehyde for the period 1914 to 1948 (19).

TABLE VI. U.S. Formaldehyde Production and Prices, 1914–1948.<sup>a</sup>

Year	Production, 1000 lb.	Price, ¢/lb.	Year	Production, 1000 lb.	Price ¢/lb.
1914.....	8,426.....	8.5	1942.....	347,463.....	5.5
1924.....	26,155.....	9.7	1943.....	522,920.....	5.5
1929.....	51,786.....	9.1	1944.....	522,440.....	5.4
1930.....	40,763.....	7.2	1945.....	509,602.....	3.2
1933.....	52,236.....	6.0	1946.....	460,048.....	3.2
1939.....	134,479.....	5.8	1947.....	615,853.....	3.6
1940.....	180,885.....	5.8	1948.....	623,838.....	3.7
1941.....	309,912.....	5.5			

<sup>a</sup> For 37% solution.  
Source: reference (19).

#### Grades, Specifications, and Shipping

Grades of formaldehyde or its polymers available at the present time are as follows: 37% N.F. formaldehyde solution; 37% low-methanol formaldehyde solution; 38–50% low-methanol formaldehyde solution; paraformaldehyde; and trioxane. The regular N.F. grade formaldehyde solution normally contains 37.0–37.3% formaldehyde by weight. Its methanol content varies from 6.0 to 15% by weight according to the requirements of the trade. The solution is slightly acid, usually containing well under 0.05% calculated as formic acid. Trace impurities include copper, usually less

than 0.5 p.p.m., and iron, less than 1 p.p.m. Total solids should approximate 50 p.p.m. or less. Organic impurities other than those listed above are usually absent from material manufactured from pure synthetic methanol. Formaldehyde or paraformaldehyde manufactured by hydrocarbon oxidation can usually be distinguished from material made from methanol by the fact that it possesses a foreign odor and gives a yellow or brown color when an approximately 37% solution is mixed with an equal volume of concentrated sulfuric acid.

Specifications for the 37% or higher-strength low-methanol solution are similar to those given above for the N.F. material, except that methanol is present to the extent of only about 1% or less. Such solutions must be kept warm as indicated under the properties of formaldehyde solution, if polymer precipitation is to be prevented. Consumers must accordingly have the special equipment (heated tanks, etc.) necessary to handle these solutions.

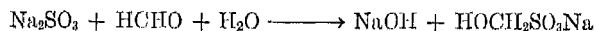
Paraformaldehyde may contain 91-98% formaldehyde by weight, the balance consisting principally of combined water. It is colorless and has an ash content of 0.1% or less. Product forms include fine, medium, granular, and flake grades. The usual commercial grade of paraformaldehyde powder contains approximately 95% HCHO. Flaked polymer, known as flake formaldehyde, may contain as low as 91% HCHO, whereas special high-molecular products may analyze over 98% HCHO. Specialty paraforms include material stabilized against the normal decrease in reactivity on aging and high-molecular material of low reactivity.

Formaldehyde is shipped in tank cars, tank wagons, drums, barrels, carboys, and bottles. Containers are preferably 18-8 stainless steel, resin-lined steel, rubber-lined aluminum, or glass. Wooden barrels are sometimes employed but may discolor the solution. However, this does not diminish strength or utility where color is not important.

Commercial formaldehyde polymers are normally shipped in wooden barrels or fiber drums. Modes of transportation for formaldehyde are freight, express, and motor truck; paraformaldehyde, hexamethylenetetramine, and trioxane may also be shipped by parcel post. The laws governing the sale of disinfectant in several states class formaldehyde as an "economic poison," but it is not considered a poison in Interstate Commerce Commission regulations. Labels for formaldehyde and paraform normally carry the warning that these materials cause irritation to skin, eyes, nose, and throat.

### Analysis

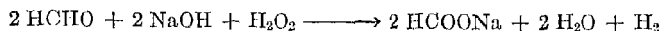
The sodium sulfite procedure and the alkaline peroxide method are, in general, the standard methods for determination of the HCHO content of formaldehyde. The sodium sulfite procedure is based on the fact that 1 mole of sodium hydroxide is liberated when 1 mole of formaldehyde reacts with sodium sulfite solution:



In carrying out this procedure, a weighed sample of commercial formaldehyde or paraform is added to a molar solution of sodium sulfite, after which the solution is titrated with normal acid using thymolphthalein or aurine as an indicator.

The alkaline peroxide procedure is based on the formation of sodium formate when formaldehyde is heated with alkaline hydrogen peroxide. The formaldehyde sample is added to a measured quantity of normal sodium hydroxide plus peroxide,

heated, and then titrated with normal acid. The quantity of sodium hydroxide consumed is proportional to the amount of formaldehyde in the sample. The chemical reaction is as follows:



An iodometric oxidation procedure as well as another technique depending on the reaction of formaldehyde with alkali cyanides, both developed by Romijn, have been almost entirely replaced by the simpler procedures described above.

The methanol content of N.F. formaldehyde is determined physically from its specific gravity and formaldehyde content or chemically by oxidation with chromic acid. In the latter method the methanol content is calculated by allowing for the chromic acid that would be required to oxidize the formaldehyde in the solution.

### Health and Safety Factors

Formaldehyde gas irritates the mucous membranes of the eyes, nose, and throat. Its solutions have a hardening or tanning action on the skin and may cause dermatitis in some cases. Some persons are hypersensitive to formaldehyde, and even a slight exposure may lead to severe reaction in such instances.

With proper precaution formaldehyde may be handled industrially with little or no difficulty, and the health hazards are not serious. The maximum permissible concentration of formaldehyde in the air as recommended by the American Standards Association is 10 p.p.m. for exposures not exceeding 8 hours daily. This figure is equivalent to 0.012 mg. per liter at 25°C. and 760 mm. Hg. Fortunately formaldehyde gas acts as its own warning agent and concentrations over 10 p.p.m. cause definite irritation. The least detectable odor is reported at 0.8 p.p.m. (1,6,7).

For optimum safety, formaldehyde solutions should be handled in closed equipment wherever possible. When this cannot be done, ventilating fans and fume hoods should be employed so that the concentration of gas in the working area will not exceed 10 p.p.m. When it is necessary for workmen to enter rooms or enclosures containing unsafe concentrations of formaldehyde, an oxygen breathing apparatus or fresh-air hose mask should be used. A cannister-type gas mask which has been approved by the Bureau of Mines for organic vapors is also satisfactory for limited use (up to 2% by volume).

Skin irritations from formaldehyde may be avoided in most cases by washing with soap and water immediately after exposure. Waterproof gloves are of value in avoiding exposure of the hands, and lanolin or related water-repellent cosmetic agents are helpful as a protection against occasional exposure. Individuals who are hypersensitive to formaldehyde should be excluded from working areas in which it is handled.

Fatal poisonings from formaldehyde have been reported only in cases where the solution was swallowed accidentally or with suicidal intent. The death of adults has been reported following ingestion of 1 oz. of 37% formaldehyde after 2½ hours to as much as 9 days. Recovery after ingestion of 4 oz. of 37% formaldehyde is reported following prompt treatment (10). A physician should be called at once in cases of formaldehyde poisoning. In general the toxic agent should be removed by gastric lavage with water. This may be followed by administration of dilute (15%) solution of ammonium acetate. This chemical converts the formaldehyde to hexamethylenetetramine. Irritation from formaldehyde may also be alleviated by the use of demulcents, for example, boiled starch, raw eggs, and milk (12).

Paraformaldehyde should be handled with the same precaution normally employed with formaldehyde solution. Masks or dust respirators should be used in handling paraformaldehyde powder. The skin, particularly the face, should be protected from accumulation of powder. In all cases where formaldehyde solution or polymers are handled, spillage of liquid or dust should be avoided. If spillage does occur, the area should be cleaned at once. Ammonia may be used to neutralize the formaldehyde, which can then be washed away with water. If extreme cleanliness is not maintained, unsafe concentrations of formaldehyde gas may develop.

### Uses

The major use of formaldehyde and its polymers is in the manufacture of synthetic resins. Of these, the phenolic resins (*q.v.*) are the chief consumer and the urea-formaldehyde resins are next in order of magnitude. Other resins include those derived from melamine, aniline, etc. (see *Amino resins and plastics*). Casein plastics used in the manufacture of buttons, buckles, etc., are hardened by treatment with aqueous formaldehyde (see *Casein*). Similar products can also be obtained from soybean protein, peanut protein, etc. (see *Protein plastics*). Glue-cork compositions in which the glue or gelatin binder is insolubilized with paraformaldehyde are employed as gasketing materials and insulators (see *Cork*). Modified vinyl resins include the formal of polyvinyl alcohol, a water-insoluble thermoplastic, often produced by reaction of polyvinyl acetate with formaldehyde in the presence of acidic catalysts (see *Vinyl compounds, resins, and plastics*).

In the textile industry, formaldehyde may be employed to improve the crease resistance and shrink resistance of rayon fabrics by treatment under acidic conditions. Severe treatment of this type produces tendering and must be avoided. Cotton is not usually treated in this way because of its sensitivity to acid. High degrees of crease resistance with relatively less tendering are produced by treatment with dimethylolurea or urea-formaldehyde condensates. Bleeding of dyes is often reduced by treating dyed textiles with formaldehyde. Considerable formaldehyde is also employed in the manufacture of formaldehyde hydrosulfite and the sulfoxylates, which are employed in dyeing and printing as stripping agents. Synthetic textile fibers are produced by the insolubilizing or stabilizing action of formaldehyde on protein filaments derived from casein, soybean protein, and peanut protein.

In the paper industry, formaldehyde finds some application for increasing wet strength, shrink resistance, grease resistance, etc. and also for increasing water resistance in coated papers. Wet strength and shrink resistance are sometimes produced by the direct reaction of formaldehyde in the presence of an acid catalyst on heating or hot-calendering. Heating in the dry state is apparently essential to produce modification. Protein sizes such as glue and casein are often insolubilized on the paper with formaldehyde to give water resistance. This same technique is also employed to insolubilize protein binders in coating compositions. Large use is also made of reactive derivatives such as dimethylolurea and methylolmelamines.

Treatment of wood with dry formaldehyde gas under acidic conditions gives a high degree of shrink resistance, but the wood is embrittled by the action of the acid catalyst.

Leather and fur can be tanned by the action of formaldehyde in the presence of buffer salts, which maintain approximate neutrality. Washable white leather can be

produced by these processes. In the fur industry, formaldehyde can be employed on sheep pelts to give the so-called mouton-type furs resembling nutria or sheared beaver, which will not curl on dyeing. The action of formaldehyde practically eliminates crimp. Syntans, usually produced by sulfonation of phenol-formaldehyde condensates, are generally employed in conjunction with other agents as assistants in the production of soft, high-grade leathers.

The action of formaldehyde on proteins also finds use in the photographic industry because of its hardening and insolubilizing action on the gelatin surfaces of sensitized films and papers. In this field the reducing action of formaldehyde on silver salts is also of value. Formaldehyde-bisulfite compositions find special use in developers for photolithography.

A large volume of formaldehyde is employed in the synthesis of derivatives such as hexamethylenetetramine (*q.v.*), pentaerythritol (*q.v.*), dimethylolurea, as well as the hydrosulfite derivatives previously mentioned. Other derivatives include methylol-melamines, rubber accelerators (such as the Schiff base anhydro-formaldehyde-*p*-toluidine (*N*-methylene-*p*-toluidine),  $(\text{CH}_3\text{C}_6\text{H}_4\text{N}:\text{CH}_2)_3$ , and the reaction product of formaldehyde and 2-mercaptobenzothiazole), *N*-phenylglycine for the manufacture of indigo, as well as innumerable drugs, dyes, surface-active compounds, insecticides, etc.

Another industrial use for formaldehyde is as an intermediate in the manufacture of ethylene glycol. Under high pressures (above 300 atm.), formaldehyde reacts with carbon monoxide and water in the presence of acidic catalysts to form hydroxyacetic (glycolic) acid (31,32). The esterification of this acid with methanol and the catalytic hydrogenation of the ester lead to ethylene glycol (34a,35,36). See *Glycols*; *Glycolic acid*.

Direct use of formaldehyde as a bactericide and disinfectant (see Vol. 2, p. 80), fungicide (*q.v.*), embalming agent, preservative, and deodorant, although originally major applications, now consume only a small percentage of the volume produced. Agricultural uses of formaldehyde include disinfection of seeds for the prevention of smut diseases, and treatment of seed potatoes to prevent scab. Wheat, oats, and barley are often subjected to formaldehyde treatment. Care should be taken to avoid undue exposure that will damage the vitality of the seed. Disinfection of seed beds with dilute formaldehyde prevents damping-off of seedlings. It is also used as a sterilizing agent in mushroom culture. Another agricultural use is found in a patented application for modifying fertilizers containing urea. By condensing with the urea, formaldehyde lowers the solubility so that the nitrogen will become available at a slower rate (34).

For disinfecting purposes, formaldehyde may be employed as a gas or in the form of a dilute solution (approximately 2%). It gives best results in gaseous disinfection when the humidity is high (about 60%). Gas may be generated by heating para-formaldehyde or by pouring the solution on an oxidizing agent such as potassium permanganate or bleaching powder. One pound of 37% formaldehyde added to 4-8 oz. of potassium permanganate generates sufficient gas to disinfect a closed area of up to 1500 cu.ft. The bactericidal action of formaldehyde coupled with its hardening action on protein makes it useful as an embalming agent. It is used for this purpose in a wide variety of embalming fluids (*q.v.*), in which it is combined with various inorganic salts, alcohol, phenol, etc. The preservative action of formaldehyde is employed in the preservation of fish for fertilizer, where it also serves as a deodorant (29). It has



many other uses as a deodorant. Dilute solutions containing small quantities of essential oils are often used to eliminate undesirable odors in public places.

Formaldehyde is a mild acid inhibitor and finds some use as a pickling addition agent in this connection. It has recently been found to be an effective inhibitor for hydrogen sulfide corrosion in oil-well equipment (2).

### Derivatives

The formaldehyde acetals (formals) are formed by the reaction of formaldehyde with alcohols in the presence of acidic catalysts. They have the type formula  $\text{CH}_2(\text{OR})_2$ , in which R is an alkyl or aralkyl radical. Methylal and dioxolane are commercially available at the present. In general, formals are characterized by their etherlike properties, resistance to alkalis, and hydrolysis to formaldehyde and the parent alcohol in the presence of acids.

**Methylal** (dimethoxymethane (I.U.P.A.C.), methylene dimethyl ether, formaldehyde dimethyl acetal, formal),  $\text{CH}_2(\text{OCH}_3)_2$ , is a colorless flammable liquid; m.p.,  $-105^\circ\text{C}.$ , b.p.  $42.3^\circ\text{C}.$ ,  $d_4^{20}$  0.86,  $n_D^{25}$  1.3504. It is soluble in approximately 3 volumes of water and infinitely soluble in alcohol and ether. It is readily produced by distillation from an acid solution of formaldehyde containing methanol, and by the reaction of paraformaldehyde and methanol in the presence of ferric chloride, zinc chloride, hydrogen chloride, etc. Methylal finds application as a special form of formaldehyde in the presence of acidic catalysts because of its solvent properties and reactivity.

**1,3-Dioxolane**, the cyclic formal of ethylene glycol,  $\text{CH}_2\text{O}.\text{CH}_2.\text{CH}_2.\text{O}$ ,  $b_{765} 76^\circ\text{C}.$ , possesses attractive solvent properties. See *Glycols*; *Solvents*.

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J. F. WALKER

**FORMALS.** See *Formaldehyde*.**FORMAMIDE**,  $\text{HCONH}_2$ . See *Formic acid*.**FORMANILIDE**,  $\text{HCONHC}_6\text{H}_5$ . See *Aniline*, Vol. 1, p. 920.**FORMIC ACID**

Formic acid (methanoic acid (I.U.P.A.C.)),  $\text{HCOOH}$ , formula weight 46.03, is the simplest of the carboxylic acids. It derives its name from *Formica rufa*, the red ant, in which it exists as the free acid. It has been known since 1670. Its occurrence in plants is widespread, and it has been detected in pine needles, the stinging nettle, and fruits. It has also been found in muscle, blood, and in capillaries.

Formic acid is a volatile liquid, giving off disagreeably pungent fumes and producing superficial blisters on contact with the skin. The formic acid of commerce is generally a 90% solution, shipped in stainless-steel drums or glass carboys. A white label is required for shipment. According to the U.S. Tariff Commission, the 1948 production of 90% formic acid was 8,500,000 lb.; the carload price was 14¢/lb. in carboys in the summer of 1950.

**Physical and Chemical Properties**

**Constants.** M.p., 8.40°C.; b.p., 100.75°C.;  $d_4^{20}$ , 1.2196;  $n_D^{20}$ , 1.3714. The vapor pressure of anhydrous formic acid is:

Temperature, °C.....	10	20	30	40	60	80	100	100.75
Vapor pressure, mm. Hg..	18.9	33.1	52.2	82.6	189.7	398.1	753.4	760

It is completely miscible with water and forms constant-boiling mixtures,  $b_{760}$  107.1°C., containing 76.5 wt. % formic acid;  $b_{1330}$  134.6°C., containing 83.2% acid; the vapor-liquid composition diagram is shown in Figure 1. The density of 90% formic acid,  $d_4^{20}$ , is 1.2045. The dissociation constant,  $K$ , of formic acid is  $1.76 \times 10^{-4}$ . This makes it a noticeably stronger acid than acetic acid,  $K = 1.75 \times 10^{-5}$ .

**Reactions.** In addition to the class reactions of a carboxylic acid (see *Acids, carboxylic*), formic acid shows certain anomalous chemical properties, since, unlike

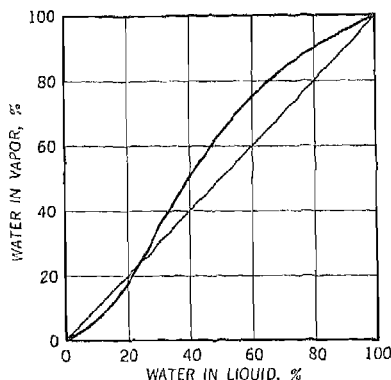


Fig. 1. Vapor-liquid composition diagram (10).

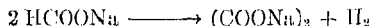
its homologs, it contains the aldehyde group, CHO. It is therefore a reducing agent of sufficient potential to reduce mercury salts to the metal or hexavalent chromium to trivalent chromium. It is readily dehydrated to carbon monoxide by concentrated sulfuric acid or by passage of its vapor over titanium or thorium oxides. Metallic catalysts, for the most part, convert formic acid vapor to hydrogen and carbon dioxide.

### Manufacture

The once classical method of preparing formic acid from oxalic acid by decarboxylation,



by heating preferably in the presence of a polyhydroxy compound, such as glycerol, is now obsolete. Formates are now made directly from alkali and carbon monoxide:

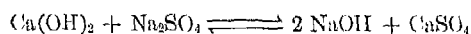


and oxalates are made by heating formates (see *Oxalic acid*): Both of these reactions were discovered by Berthelot. In recent years a substantial amount of by-product sodium formate has been available from the process for manufacturing pentaerythritol from formaldehyde and acetaldehyde. Formic acid is therefore manufactured from sodium formate and an inorganic acid. Many proposals for a direct synthesis of formic acid from carbon monoxide and steam have appeared in the patent literature. None of these has attained technical success (see p. 878).

### MANUFACTURE OF FORMATES

The first technical application of the Berthelot reaction was carried out by Goldschmidt, who treated soda lime with carbon monoxide under pressure. Elektrochemische Werke Bitterfeld by the use of a suitable agitator-equipped autoclave applied this procedure to lumps of solid caustic soda. Both of these processes are obsolete, but for technical details and apparatus see reference (12).

The reaction may be carried out by using aqueous alkali. A slurry of hydrated lime in sodium sulfate solution is treated with carbon monoxide. The slurry is, of course, in equilibrium with calcium sulfate and caustic soda.



The calcium sulfate so obtained is difficult to filter and wash. Moreover, its solubility in sodium formate solution is higher than in water, and if the sodium formate is to be converted to oxalate, the presence of even small amounts of calcium adversely affects the conversion.

**Sodium Formate from Caustic Soda.** With the present low cost of alkali, it is

simpler and cheaper to make sodium formate directly from aqueous sodium hydroxide and producer gas containing approximately 33% carbon monoxide.

Modern processes are continuous. Since the absorption of carbon monoxide by caustic soda is a slow reaction, an appreciable period of time must be allowed for the gas to be in contact with the liquor. The advantage of countercurrent flow, whether through a battery of autoclaves or other devices, is obvious. Producer gas is cleaned, compressed to 200–250 p.s.i., and passed through a 25–30% sodium hydroxide solution in countercurrent flow at 160–200°C. The waste gas, stripped of its carbon monoxide but containing steam, passes out through a heat exchanger to the exhaust. The effluent liquor is evaporated to dryness to obtain the sodium formate. The dry sodium formate may then be used either for the manufacture of formic acid, or for conversion to sodium oxalate. A sizable quantity of sodium formate is also sold as such.

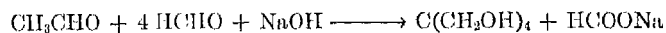
Sodium formate is widely used in the chrome tanning of leather, and, by reaction with aluminum salts, in the waterproofing of washable wall paper.

**Calcium Formate.** It has been proposed that milk of lime be substituted for caustic soda to produce calcium formate for conversion to formic acid. Fischer, Tropsch, and Schellenberg studied this reaction in an autoclave (8). They found that the reaction of 8 *N* milk of lime with pure carbon monoxide at 160°C. required 12–17 hours for completion and that at 180°C. the iron parts of the autoclave were attacked. Obviously the low solubility of calcium hydroxide and the correspondingly low concentration of hydroxyl ion places a serious limitation on the speed of the reaction. Fischer and Philippovich studied the reaction between carbon monoxide and other alkalis (7).

**Formates from Lime and Alkali Sulfates.** The disadvantages in converting a slurry of lime in sodium sulfate solution to sodium formate have already been mentioned. However, it has been claimed that if 10% of sodium formate is present in the lime slurry before starting, the calcium sulfate will be precipitated in larger crystals from which the sodium formate liquor is easily separated (17).

When potassium sulfate is used, the process is further complicated by the precipitation of the insoluble double salt  $K_2SO_4 \cdot 5CaSO_4$ , which must be worked up for recovery of potassium sulfate.

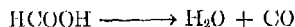
**By-Product Sodium Formate.** In the technical process for making pentaerythritol (*q.v.*) (see also Vol. 1, p. 322), one mole of formate is formed for each mole of pentaerythritol:



In recent years this has supplied significant quantities of the sodium formate on the market.

#### FORMIC ACID FROM SODIUM FORMATE

The conversion of sodium formate to formic acid is carried out subject to two limitations. One is the breakdown of formic acid in the presence of concentrated sulfuric acid according to the equation:



This takes place even at room temperature and is almost instantaneous at higher temperatures. If dilute sulfuric acid is used to produce dilute formic acid, the latter cannot be concentrated by simple fractional distillation due to the second limitation,

namely, the existence of a constant-boiling formic acid–water mixture, which at atmospheric pressure contains only 76.5% acid (see Fig. 1). The traditional method therefore calls for making a slurry of sodium formate in an equal weight of 90% formic acid. To this slurry sulfuric acid must be cautiously added, with cooling, until the equivalent amount is added, after which the formic acid may be distilled off. This process is customarily carried out in a steam-jacketed acidproof still equipped with an agitator of sufficiently close clearance to scrape sodium sulfate scale away from the still wall. Although sodium formate and formic acid form acid salts,  $\text{HCOONa.HCOOH}$  and  $3\text{HCOONa.HCOOH}$ , these melt at temperatures below distillation (25). However, unless the sulfuric acid is added with great care, the appreciable heat of dilution results in some decomposition as well as loss by premature volatilization. When the addition of sulfuric acid is finished, the formic acid may be distilled off, either at atmospheric pressure or at reduced pressure. It is then redistilled, diluted to 90%, and packaged. The finished acid is shipped in 12-gal. glass carboys.

The sodium sulfate residue is suitable for use in making Kraft pulp and paper and, if the heavy-metal content is kept low, for glass manufacture.

Neumann claims the process of making formic acid from phosphoric acid and sodium formate. The residue of monosodium phosphate finds a ready demand. However, this process requires 100% phosphoric acid or else offers the problem of concentrating the formic acid made from the 85% phosphoric acid of commerce.

#### FORMAMIDE PROCESS

Meyer and co-workers have developed a process based upon the reaction of carbon monoxide and ammonia (9,14–16,23,24). Carbon monoxide or gas containing carbon monoxide at 150–200 atm. is treated with ammonia at 200°C. or thereabouts to give formamide. If enough water is present, a mixture of formamide and ammonium formate is formed. A paste of ammonium formate and formamide is treated with sulfuric acid by running the latter in with cooling, and the formic acid is distilled off, the last part of it in vacuum, leaving a residue of by-product ammonium sulfate.

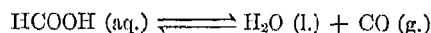
This process has undergone considerable further development by the I. G. Farbenind. in Germany (9,18,27). It is also possible to make formamide via methyl formate: carbon monoxide reacts with methanol catalytically under high pressure to form methyl formate, which is treated with ammonia giving formamide and regenerated methanol.

It has been reported that formic acid has been manufactured from formamide in the U.S.

#### DIRECT SYNTHESIS OF FORMIC ACID

There are a number of processes in the patent literature for the direct synthesis of formic acid from carbon monoxide and water or steam. Due consideration of the available free-energy data would have made clear to the patentees that only a dilute aqueous formic acid could be expected, even if equilibrium were attained at pressures that could be realized in practice.

The free energy of formic acid has been recalculated by Lewis and Randall from the equilibrium measurements of Branch (2). They find that for the reaction:



the activity quotients (equilibrium constants to a first approximation) are: 156°C.,  $K = 85$ ; 218°C.,  $K = 264$ .

$$K = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{HCOOH}]}$$

$$\Delta F_{298}^0 = -1150$$

In the above:

$$[\text{H}_2\text{O}] = \frac{\text{Fugacity of water in soln.}}{\text{Fugacity of pure water}}$$

Thus  $[\text{H}_2\text{O}]$  is always less than 1. It is nearly 1 for a dilute solution. Therefore:

$$\frac{\text{Pressure CO (atm.)}}{\text{Concn. HCOOH (moles/kg. H}_2\text{O)}} \cong 85 \text{ at } 156^\circ\text{C.}$$

Obviously more refined calculations are not required to show that 90% formic acid cannot be obtained by direct synthesis at pressures that would be practical. However, the use of cuprous halides as catalyst for this reaction has been claimed.

A series of patents on this process assigned to Du Pont were issued as follows: to Vail using boron phosphate as catalyst at 700 atm. claiming 50% conversion (29), to Woodhouse using halogen or sulfur or phosphorus at 400°C. and 700 atm. (36), and to Carpenter using a variety of catalysts (34,35,37). Patents on the direct synthesis were also issued to Dreyfus (38). More recently references to this process have appeared in England (3,4). In view of the thermodynamics of the reaction it is difficult to see how any of the above constitute a workable process.

#### ANHYDROUS FORMIC ACID

Convenient quantities of anhydrous or nearly anhydrous formic acid for laboratory use can be made either by freezing out crystals of formic acid from 90% formic acid, or by rectification in an efficient packed column several feet in length. Ritter converts 85% formic acid and aniline to formanilide, distills off the water, and hydrolyzes the formanilide with careful cooling by sulfuric acid and the equivalent quantity of water (11). He has obtained 90% yields of nearly anhydrous formic acid by this method.

The methods depending on dehydration by solid drying agents, for example, anhydrous copper sulfate or magnesium sulfate, do not give good enough yields to be practical. The same may be said of the method of Rohde, which uses acid anhydrides, for example, phthalic or boric anhydride (27a).

The technically suitable methods are essentially distillation methods. Where only a limited part of the formic acid produced must be dehydrated, a simple rectification in a bubble-cap column will separate strong formic acid into anhydrous acid and 77% formic acid. For the McCabe-Thiele diagram for this binary system see Figure 1 (10). Where all the formic acid produced must be dehydrated, either azeotropic distillation or chemical regeneration must be used. A carefully worked out azeotropic distillation process is that of Clarke and Othmer using propyl formate as the entraining liquid (26,33). The distillate contains about 9% water and separates into two phases, of which the aqueous phase contains less than 1% formic acid. When phase separation ceases, the remaining binary mixture of propyl formate-anhydrous formic acid may be separated by distillation. See also references (13,19,22,30,31,42).

Another distillation method is based on the addition of a high-boiling or non-

volatile compound to form a loose addition compound with the formic acid, so that water may first be distilled off, followed by distillation of the formic acid. Compounds recommended include such tertiary bases as trimethylamine (40), quinoline, picoline, or dimethylaniline (20,32); a tertiary base and an entraining liquid (instead of vacuum distillation) (21,39); and sodium formate (distillation at 10–20 mm. is claimed to give an 80% yield of 98% formic acid) (28). Guinot and Chassaing have devised a countercurrent extraction method using methyl-substituted tetrahydrofuran. A 15% aqueous solution of formic acid is completely deacidified and anhydrous formic acid is recovered by distillation (41). In addition to the regeneration method of Ritter already described, there is a method in which methyl formate is treated with glutaric acid. After distilling off the formic acid, the methyl glutarate may be hydrolyzed. The large number of methods proposed suggests that no one is wholly satisfactory.

### Materials of Construction and Health and Safety Factors

In earlier practice, cast iron, Duriron (a silicon-containing cast iron), and stoneware were used. More recently, industrial glass pipe, glass-lined vessels, impregnated carbon, and molybdenum-containing stainless steel, such as type 316, have been used.

Formic acid in contact with the skin will produce blisters almost instantly. The fumes too are extremely irritating. Consequently, rubber gloves and goggles should always be worn when handling formic acid. Adequate ventilation should be provided, just as for hydrochloric acid. In case of contact, immediate flushing of skin and eyes with water for fifteen minutes is important. For eyes medical attention should be obtained.

### Analysis and Specifications

Formate is usually determined by alkaline oxidation with standard potassium permanganate. An alkaline aliquot containing approximately 30 mg. sodium formate is heated with an excess of 0.2 *N* permanganate to 70°C.; 20 ml. 20% potassium iodide solution is added and back-titrated immediately with 0.1 *N* sodium thiosulfate.

$$1 \text{ ml. } 0.2 \text{ N KMnO}_4 = 0.0068 \text{ gram HCOONa} = 0.0046 \text{ gram HCOOH}$$

The standards for technical (90%) formic acid as set up by one manufacturer are given in Table I. Formic acid is listed in the N.F. IX. The N.F. grade is an aqueous solution containing not less than 24 and not more than 26% formic acid.

TABLE I. Specifications for 90% Formic Acid.

	Specification	Analysis
Acidity.....	90.4–90.8%	90.6%
Lead.....	Less than 20 p.p.m.	3 p.p.m.
Sulfate.....	None	None
Iron.....	Less than 3 p.p.m.	2.5 p.p.m.
Chlorine.....	Trace	None
Total solids.....	Less than 0.025%	0.010%
Color.....	Water white	Water white
Water solution.....	Clear	Clear

### Uses and Applications

The bulk of the formic acid of commerce is consumed by the textile industry, either in dyeing or textile finishing. Since it is a volatile acid, it does not remain on the fiber on drying like sulfuric acid. Since it is a stronger acid than acetic acid, it gives a better exhaustion of the dye bath in acid and chrome dyeing. As a reducing agent, it functions in chrome dyeing to reduce hexavalent to trivalent chromium for mordanting. By requiring a smaller amount of chromium due to more complete reduction, a softer feel is imparted to the goods. In the dyeing of mixed goods, the substitution of formic acid for sulfuric acid avoids degradation of the cellulose, which is appreciable below pH 3. For the application of many dyes, the pH of a formic acid solution gives the correct range for slow enough exhaustion to give level shades, together with sufficiently complete exhaustion to be economical.

Another textile application is in scrooping. This is a treatment with a formic acid and tallow-soap bath to impart a suitable "feel" to the finished cotton cloth. In recent years, formic acid has come into use for the discharging of melamine resins on fabric for shrinkproofing and wrinkleproofing. See *Dyes (application)*; *Textile technology*.

Formic acid can be used instead of formaldehyde in the preparation of acridine, 3,6-diaminoacridine, and the following acridine dyes: Acridine Yellow (C.I. 785), Auracine G (C.I. 786), and Acridine Orange NO (C.I. 788).

Formic acid is generally preferred for acid coagulation of rubber latex. In leather manufacture, formic acid is used for delining, that is, neutralizing the lime. Used for this purpose, it gives a superior feel and plumpness to the leather and, since it is volatile, any excess does not remain in the leather. When formic acid is used as a laundry sour, its volatility obviates the necessity for a rinse after the sour bath.

Formic acid is used in nickel-plating baths, and in wire-stripping compounds. The latter are applied in de-enameling magnet wire in the process of reclaiming motor windings, and in the preparation of bare wire for soldering.

Formic acid is also used as an acid catalyst in the manufacture of phenolic resins.

### Derivatives

For metal formates see such headings as *Aluminum compounds*; for esters, see *Esterification*; *Esters, organic*, Vol. 5, pp. 826, 841; for performic acid (peroxyformic acid), see *Peroxides and peroxy compounds* and references (5,6,43). See also *Carbonic and chloroformic esters*.

**Formamide** (methanamide (I.U.P.A.C.)),  $\text{HCONH}_2$ , formula weight 45.04, is the only amide liquid at ordinary temperatures. It is a colorless, odorless, hygroscopic, slightly viscous liquid; m.p.  $2.5^\circ\text{C}$ .,  $b_{30}$   $129^\circ\text{C}$ .,  $b_{760}$   $210^\circ\text{C}$ . (dec.),  $d_4^{20}$  1.1339,  $n_D^{16}$  1.4491. Formamide is unusual among organic compounds in that it has a high dielectric constant (more than 80) and is thus an excellent ionizing solvent. It is soluble in water, lower alcohols, and glycols, and insoluble in hydrocarbons, chlorinated solvents, and ethers. It dissolves casein, gelatin, zein, animal glue, and related water-soluble gums and resins, and is a good solvent for a number of inorganic salts. On heating with alcohols, it gives formic esters; with formaldehyde, formamide forms methylol and methylene derivatives.

Formamide is prepared by heating crystallized ammonium formate in a sealed



tube at 230°C. or by heating anhydrous ammonium formate at 100-180°C. and distilling at 0.5 mm. in an atmosphere of ammonia. It may also be prepared by the high-pressure reaction between ammonia and carbon monoxide, partial hydrolysis of hydrogen cyanide, or ammonolysis of formate esters, particularly methyl formate. This ester is made by high-pressure synthesis from carbon monoxide and methanol (see Vol. 5, p. 797).

Formamide has found technical use as a source of hydrogen cyanide (see Vol. 4, p. 693) and of formic acid, as a softener for glue, paper, and polyvinyl alcohol, and as a solvent in the steam-set type of printing inks. It is also used as a solvent for nylon and as a soldering flux.

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BENJAMIN TOUBES

**FRANCIUM.** See "Element 87" under *Elements*.

**FRANKLINITE,** (Fe,Zn,Mn)O.(Fe,Mn)<sub>2</sub>O<sub>3</sub>. See *Iron*.

**FRARY METAL.** See *Bearing metals*, Vol. 2, p. 373; *Leul alloys*.

**FREE ENERGY.** See *Electrochemistry*, Vol. 5, p. 497; *Thermodynamics*.

**FREE RADICALS.** See *Radicals*.

**FREEZING POINT.** See *Melting and freezing temperatures*.

**"FREON" COMPOUNDS.** See "Fluorinated hydrocarbons" under *Fluorine compounds, organic*; *Refrigeration*.

**FRICTION FACINGS.** See *Brake linings and other friction facings*.

## FRIEDEL-CRAFTS REACTION

In 1877, Charles Friedel and James Crafts reported the action of metallic aluminum on amyl chloride. As a result of this work and their later investigations, including studies of the action of aluminum chloride on amyl chloride and on a mixture of amyl chloride and benzene (to produce amylbenzene), the name Friedel-Crafts has been applied to reactions brought about by the use of anhydrous aluminum chloride or other inorganic halides. In the papers on their new synthetic method, these investigators described such diverse applications as the reactions of organic halides, anhydrides, acids, oxygen, sulfur, carbon dioxide, sulfur dioxide, sulfur chloride, and phosphorus halides with aromatic hydrocarbons. The hydrocarbons included benzene, toluene, xylene, durene (1,2,4,5-tetramethylbenzene), ethylbenzene, diphenyl (biphenyl), and naphthalene.

The term Friedel-Crafts reaction has been used to cover a wide variety of reactions, from two main types to a large number. In view of the possible extremely broad scope of the reactions, some writers prefer to use the name Friedel-Crafts syntheses. In the most restricted (and probably more usual) sense, Friedel-Crafts reaction denotes only substitution of nuclear hydrogen in aromatic or heteroaromatic (heterocyclic) compounds to form (1) hydrocarbons and their derivatives or heteroaromatic derivatives (by alkylation) or (2) ketones and aldehydes (by acylation). In a broader sense, the term includes other reactions catalyzed by aluminum chloride and certain other halides. Other catalysts than anhydrous aluminum chloride that bring about reactions of similar types are anhydrous ferric chloride, hydrogen fluoride, sulfuric acid, boron trifluoride, stannic chloride, phosphoric acid, zinc chloride, and antimony pentachloride. Reactions brought about by these other catalysts have been classified by some workers as modified Friedel-Crafts reactions (33), although for this article modified Friedel-Crafts reactions will be considered to include (regardless of the catalyst used) reactions such as alkylation of isoparaffins and cycloparaffins with olefins, reactions of aliphatic hydrocarbons with acyl halides to form ketones, isomer-

TABLE I. Typical Friedl-Crafts Syntheses.

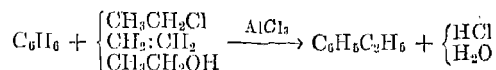
Reactant 1	Amount used, moles	Reactant 2	Amount AlCl <sub>3</sub> , moles	Solvent	Time, hr.	Temp., °C.	Product	Yield, %	Ref.
Alkylation Reactions									
C <sub>6</sub> H <sub>6</sub>	6.7	CCl <sub>4</sub>	14.5	3.4	15	5-10	C <sub>6</sub> H <sub>5</sub> CCl <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	87	(29)
C <sub>6</sub> H <sub>6</sub>	5	CH <sub>3</sub> :CH <sub>2</sub>	10	0.4	48-72	70-90	C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	60	(30)
C <sub>6</sub> H <sub>6</sub>	350 ml.	C <sub>6</sub> H <sub>5</sub> CHBrCOCH <sub>3</sub>	0.276	0.56	2	80	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCOCH <sub>3</sub>	57	(38)
C <sub>3</sub> H <sub>7</sub> CH <sub>3</sub> <sup>a</sup>	0.75	CH <sub>3</sub> :CHCH <sub>3</sub>	0.55	0.075 AlBr <sub>3</sub> + 10 ml./min. HBr	2	-42	1,2-C <sub>6</sub> H <sub>10</sub> (CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )	53	(31)
C <sub>10</sub> H <sub>8</sub>	2.0	HO(CH <sub>2</sub> O) <sub>n</sub> H <sup>b</sup>	110 g.	165 ml. H <sub>3</sub> PO <sub>4</sub> (85%) + 4.2 moles HCl	6	80-85	C <sub>10</sub> H <sub>7</sub> CH <sub>2</sub> Cl	74	(20)
Syntheses of Ketones and Aldehydes									
C <sub>6</sub> H <sub>6</sub>	2.5	(CH <sub>3</sub> CO) <sub>2</sub> O	2.0	5.6	2	Reflux	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	83	(1)
C <sub>6</sub> H <sub>5</sub> Cl	2.5	(CH <sub>3</sub> CO) <sub>2</sub> O	2.0	5.6	2	Reflux	p-ClC <sub>6</sub> H <sub>4</sub> COCH <sub>3</sub>	78	(1)
C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	2.5	(CH <sub>3</sub> CO) <sub>2</sub> O	2.0	5.6	2	Reflux	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COCH <sub>3</sub>	94	(1)
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	2.5	(CH <sub>3</sub> CO) <sub>2</sub> O	2.0	5.6	2	Reflux	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> COCH <sub>3</sub>	89	(1)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COCl	0.2	—	14.5	0.23	0.1	Reflux	C <sub>10</sub> H <sub>10</sub> O <sup>c</sup>	91	(28)
S <sub>2</sub> CH:CH:CH:CH <sup>d</sup>	0.2	CH <sub>3</sub> COCl	14.5	0.2 SnCl <sub>4</sub>	1.5	0	S <sub>2</sub> CH:CH:CH:CH:COCH <sub>3</sub>	83	(23)
C <sub>6</sub> H <sub>6</sub>	2.24	CO:CH:CH:CO	0.347	0.75	1.3	80	C <sub>6</sub> H <sub>5</sub> COCH:CHCOOH	85	(21)
C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> <sup>e</sup>	0.48	(CH <sub>3</sub> CO) <sub>2</sub> O	0.48	0.96	1	Reflux	2-CH <sub>3</sub> COCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	95	(35)
C <sub>6</sub> H <sub>5</sub> NHCOCH <sub>3</sub>	1.5	ClCH <sub>2</sub> COCl	2.66	4.5	0.5	Reflux	p-ClCH <sub>2</sub> COCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NHCOCH <sub>3</sub>	83	(27)
Miscellaneous Syntheses									
C <sub>6</sub> H <sub>6</sub>	16	S <sub>2</sub> Cl <sub>2</sub>	3.0	3.48	3	10-30	C <sub>6</sub> H <sub>5</sub> SC <sub>2</sub> H <sub>5</sub>	83	(22)
C <sub>6</sub> H <sub>6</sub>	1.1	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SeCl <sub>2</sub>	0.13	0.22	3	10-20	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SeCl	67	(26)
C <sub>6</sub> H <sub>5</sub> OH	2.0	CH <sub>3</sub> COCH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	2.0	4.0	0.5	100	C <sub>6</sub> H <sub>4</sub> :C(CH <sub>3</sub> ):CH:CO:O <sup>f</sup>	85	(25)

<sup>a</sup> Methylcyclopentane. This reaction to give a cyclohexane derivative is included as an example of a modified Friedel-Crafts reaction. <sup>b</sup> Paraformaldehyde (see Vol. 6, p. 861). <sup>c</sup>  $\alpha$ -Tetralone (3,4-dihydro-1(2H)-naphthalenone. <sup>d</sup> Thiophene. <sup>e</sup> Fluorene. <sup>f</sup> 4-Methylcoumarin.

ization of hydrocarbons, polymerization of unsaturated hydrocarbons, and reactions of unsaturated compounds with hydrogen halides and alkyl halides to form halohydrocarbon derivatives. See also *Alkylation; Hydrocarbons; Petroleum*.

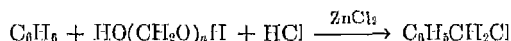
In this article then, Friedel-Crafts reaction will be used to include reactions of aromatic hydrocarbons and their derivatives or heteroaromatic compounds (all of which are electron donors) with compounds such as ethyl chloride, carbon tetrachloride, ethylene, ethyl alcohol, acetyl chloride, and carbon monoxide (which are electron acceptors) in the presence of an acidic reagent (according to the Lewis system—see Vol. 1, pp. 134–37), usually a metallic or metalloid halide, which activates the electron acceptor. The chief reactions may be classified as follows:

*Alkylation* (hydrocarbon synthesis): (a) Alkylation of aromatic hydrocarbons and other aromatic and heteroaromatic compounds (for example, phenols and thiophene), with alkyl halides and certain other aliphatic halogen compounds, olefins, alcohols, and ethers:

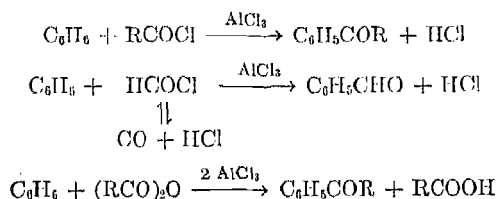


Since in most cases the reaction does not stop with the introduction of one alkyl group, mixtures of products result. Furthermore, the reaction is reversible so that transfer of alkyl groups sometimes takes place. The alkyl groups themselves often also rearrange (see p. 886).

(b) Chloromethylation of aromatic compounds (14): Replacement of a nuclear hydrogen of aromatic hydrocarbon and various derivatives with the chloromethyl group in which paraformaldehyde and hydrochloric acid or chloromethyl ether is used as a source of chloromethyl groups and aluminum chloride, zinc chloride, sulfuric acid, or hydrogen chloride is used as catalyst.

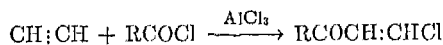


*Synthesis of Ketones and Aldehydes:* Reactions of aromatic compounds with acyl halides (or carbon monoxide with or without hydrogen chloride), acid anhydrides, and esters:



Reactions of this type are generally more satisfactory than the hydrocarbon syntheses because they stop after one acyl group has been introduced, and no rearrangement takes place. High yields of pure products can usually be obtained.

Reactions of unsaturated aliphatic hydrocarbons with acyl halides are similar and might be classed as modified Friedel-Crafts reactions; for example:



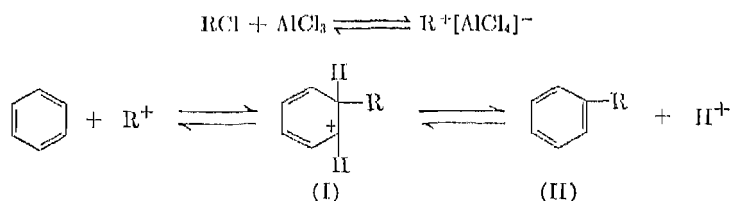
Further examples of Friedel-Crafts reactions may be found in Table I.

Many excellent articles and books on this subject have appeared (4,5,6,10,11,16,17,33,40). Particularly recommended are the *Chemical Reviews* article by Calloway (6) and the much more extensive book by Thomas (40).

## Mechanism of Reaction

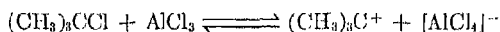
The mechanisms of Friedel-Crafts syntheses have been the subject of much conjecture and experimentation. The following discussion is but a brief summary of more recent explanations.

The carbonium-ion concept appears to be the best general theory to explain the large variety of reactions catalyzed by the metallic and metalloid halides (3,12,34,37, 41). It is believed that the acidic catalyst and the electron-acceptor reactant form, by means of coordinate valence, a polarized complex, one ion of which is a carbonium ion. Reaction can then occur by addition of the electron-deficient carbonium ion to a molecule of the electron-donor reactant to form another carbonium ion, or the original carbonium ion may rearrange and then add. The final carbonium ion, which in the alkylation of benzene, for example, has a pseudoaromatic structure (I), can then be converted to the product (II) by reaction with any base (such as chloride ion), which removes a proton (32):



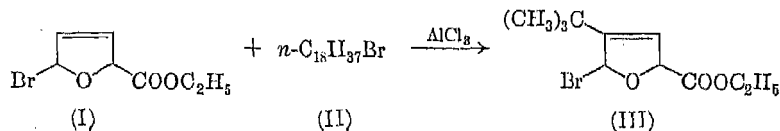
Similarly, in acylation reactions, acyl halides form carbonium ions of the type  $\text{RC}^+\equiv\text{O}$ , probably through intermediate oxonium compounds such as  $\text{RC}(\text{Cl})=\text{O}^+\text{AlCl}_4^-$ . The formation of oxonium compounds explains the need of more than catalytic amounts of aluminum chloride in acylation (see p. 887). See also *Carbonium ion*, Vol. 3, p. 156; *Catalysis*, Vol. 3, p. 260.

Some experimental evidence of the truth of the above theory has been published by Fairbrother (12), who suggested that in Friedel-Crafts reactions involving acyl and alkyl halides the coordination compounds formed contain the anion  $[\text{AlCl}_4]^-$ :



All the chlorine atoms of the anion should have an equal chance of escaping as hydrogen chloride. This was confirmed by using aluminum chloride containing radioactive chlorine as the catalyst for the reaction of *tert*-butyl chloride with benzene. The hydrogen chloride evolved contained radioactive chlorine.

As indicated above, the carbonium ion may rearrange during alkylation. At the same time, cleavage of the alkyl group often occurs. An extreme case of this phenomenon is illustrated with ethyl 5-bromo-2-furoate (I), which on alkylation with *n*-, iso-, or *tert*-butyl halide gives the same product, ethyl 4-*tert*-butyl-5-bromo-2-furoate (III) (15); even more surprisingly the same product is obtained by using *n*-amyl chloride, *n*-hexyl bromide, and even *n*-octadecyl bromide (11):



### Catalysts

Because of its availability and low cost (\$0.11/lb. in May 1950), resublimed aluminum chloride has been the most generally used catalyst in industrial Friedel-Crafts syntheses. In this discussion the usual formula  $\text{AlCl}_3$  will be used, although vapor densities show that up to  $440^\circ\text{C}$ . aluminum chloride exists as the double molecule  $\text{Al}_2\text{Cl}_6$  (see Vol. 1, p. 632). With other metal halides it frequently forms double halides, and those formed with sodium chloride are commonly used because of economy and low melting point. The compound  $\text{AlCl}_3\cdot\text{NaCl}$  is fluid at  $141^\circ\text{C}$ . (24) and is convenient for some reactions. Small traces of impurities markedly alter both the yield and direction of the reaction. The impurity which is most often present in aluminum chloride is ferric chloride. In proportion to its amount ferric chloride decreases the yield of product in the reactions of benzene with carboxylic acid chlorides and with an excess of carbon tetrachloride (36). Yields from reactions of an excess of benzene with anhydrides and with carbon tetrachloride were at first decreased by the addition of ferric chloride to the aluminum chloride, then rose to a maximum at 50 mole % of ferric chloride, and finally decreased to the yield obtained with pure ferric chloride.

In general, it is desirable to exclude moisture from reactions involving anhydrous aluminum chloride. However, in some cases, traces of moisture show an accelerating effect, probably due to the released hydrogen chloride which is known to aid such reactions. This effect is noted principally in the reactions of aromatic hydrocarbons with olefins.

Comparison of the activity of the many catalysts available has frequently been made. One such list in decreasing order of activity is based on the reaction of benzene with ethylene (19):  $\text{AlCl}_3$ ,  $\text{ZrCl}_4$ ,  $\text{TaCl}_5$ ,  $\text{CbCl}_5$ ,  $\text{BeCl}_2$ ,  $\text{TiCl}_4$ . Another series based on the reaction of benzene with acetyl chloride is (9):  $\text{AlCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{FeCl}_3$ ,  $\text{TeCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{TeCl}_4$ ,  $\text{BiCl}_3$ ,  $\text{ZnCl}_2$ .

Aluminum bromide,  $\text{AlBr}_3$ , although expensive, is said to have advantages over aluminum chloride because of its greater solubility in organic solvents, particularly alkanes. Boron trifluoride and anhydrous hydrogen fluoride are becoming increasingly important in recent years as Friedel-Crafts catalysts (see *Fluorine compounds, inorganic*).

Depending on the type of reactants, the quantity of catalyst may vary from catalytic to stoichiometric amounts. In alkylations with halides and olefins, it is required in only catalytic amounts (about 1–10%). On the other hand, in acylations with acyl halides and anhydrides, at least one mole of aluminum chloride per mole of halide or anhydride is used. It is necessary to use one mole of aluminum chloride with primary alcohols, and somewhat less with secondary and tertiary alcohols (33).

### Solvents

In industrial applications where a solvent is necessary, it is desirable to use an excess of one of the reactants, thus simplifying recovery. If neither reactant is a liquid at the temperature used, an inert diluent is employed. The selection of the diluent is very important. Many solvents modify the activity of the catalyst to a considerable extent by formation of complexes. For example, attempted acylation of phenol with phthalic anhydride in carbon disulfide with aluminum chloride catalyst results in excessive acylation and tarry products. However, substituting nitrobenzene for carbon disulfide as solvent permits the formation of the keto acid desired. If tetrachloro-

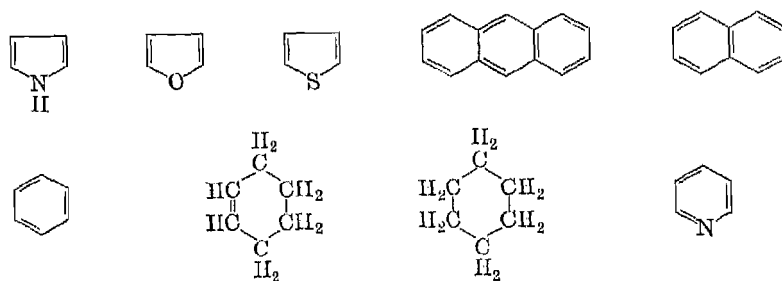
ethane is used as a solvent, a still greater yield of the product is obtained. The reaction of phosgene with benzene in the presence of aluminum chloride with carbon disulfide as diluent permits the isolation of the intermediate benzoyl chloride-aluminum chloride complex due to the insolubility of the complex in the carbon disulfide. If an excess of benzene is used as solvent, the reaction proceeds to benzophenone. The formation of such complexes with the solvent brings about a solution of the aluminum chloride, permitting homogeneous reaction conditions which are generally desirable.

Another effect of solvents noted in certain Friedel-Crafts reactions is the difference in their directive influence. For example, naphthalene will acylate in the alpha position with acetyl chloride if carbon disulfide or tetrachloroethane is used as solvent. However, if nitrobenzene is used as solvent, naphthalene acylates in the beta position.

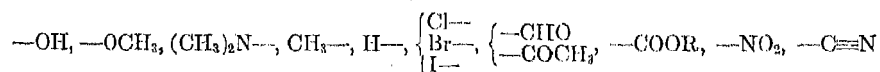
In addition to the reactants themselves, common solvents used are carbon disulfide, methyl chloride, carbon tetrachloride and other chlorides, nitrobenzene, and the nitroparaffins. In the nitroparaffins, aluminum chloride is very soluble, as much as 50%. They have been used extensively in recent years, but there are possible explosion hazards (8).

### Activating and Inhibiting Groups

The case of alkylation and acylation by means of the Friedel-Crafts reaction is dependent on many factors, of which some of the most important are the structure of the compound being alkylated or acylated, the type of groups with which it is substituted, and also the nature of the alkylating or acylating agent. Calloway has arranged various unsubstituted rings in the approximate order of decreasing activity (6):



He also lists the substituents in the approximate order of decreasing effect on the activity of the ring compound:



In general, an increasing electronegativity of the group increases the difficulty of substitution. Orientation usually follows the rules of classical organic chemistry (see Vol. 2, p. 424).

The nature of the alkyl or acyl group is very important in its effect on the reactivity of the alkyl and acyl halides. The relative reactivity of these halides is also conditioned by the halogen. For example, in aluminum chloride-catalyzed alkylations with either *n*-butyl or *tert*-butyl halides, the order of activity as reported by Calloway is  $\text{F} > \text{Cl} > \text{Br} > \text{I}$  (7). This order of activity was also noted for the hydrogen fluoride-

catalyzed alkylation of benzene with cyclohexyl and *sec*-octyl halides (39). The order of activity for the corresponding acyl halides is the reverse of the above (7).

### Laboratory Applications

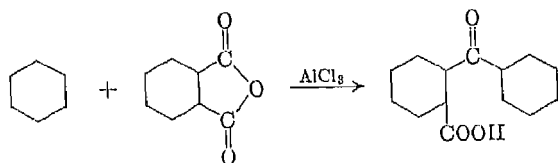
Since its discovery, the Friedel-Crafts reaction has been a valuable tool in the laboratory as well as in industrial synthesis of a large variety of organic compounds, possibly exceeded in versatility only by the Grignard reaction. In Table I is given a summary of some of the Friedel-Crafts reactions to be found in *Organic Syntheses* (which gives a wealth of detail for easily reproducible processes) and several examples from other sources. The yields are the highest figure where a range of yields was indicated.

### Industrial Applications

In the conversion of petroleum products to high-octane gasoline and other desirable products by alkylation, isomerization, and polymerization, the modified Friedel-Crafts type of synthesis has probably found its largest use. See *Alkylation*; *Hydrocarbons*; *Petroleum*.

Undoubtedly, the single pure chemical manufactured in the greatest amount by this synthesis is ethylbenzene, used in the manufacture of styrene for rubber, plastics, and chemical syntheses (see *Alkylation*, Vol. 1, p. 543; "Ethylbenzene" under *Hydrocarbons*; *Styrene*).

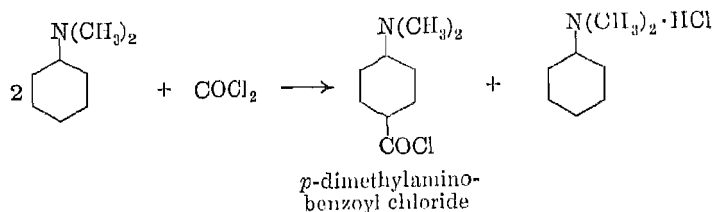
The Friedel-Crafts synthesis finds its most diversified applications in the dye industry. In the U.S., practically all anthraquinone and substituted anthraquinones are manufactured by the acylation of benzene and its derivatives by means of phthalic anhydride. Benzoylbenzoic acids are formed, which are then converted to the anthraquinone derivative by dehydration with sulfuric acid. Process details are given under anthraquinone (*q.v.*) for the manufacture of the intermediate *o*-benzoylbenzoic acid in 96% yield by the following scheme:



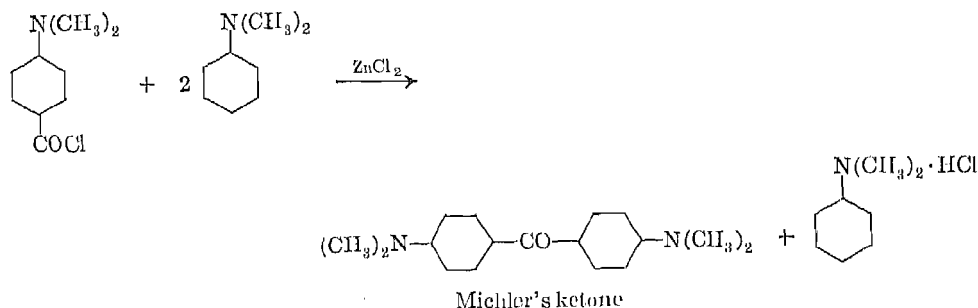
In general, the alkyl- and halogen-substituted anthraquinones are prepared by using substituted benzenes such as toluene, xylenes, and mono- and dichlorobenzenes (see Vol. 1, pp. 948, 954; Vol. 5, p. 340). Less frequently, substituted phthalic anhydrides are used.

In addition to the intermediates for anthraquinones, many other dye intermediates may be manufactured by the use of Friedel-Crafts syntheses. Some of these are: acetophenone (*q.v.*), benzaldehyde (*q.v.*), alkyl phenols, aromatic acids, benzophenone (*q.v.*), and their derivatives. An important intermediate in the synthesis of triphenylmethane dyes (*q.v.*) is Michler's ketone, which is manufactured in two steps, the second involving a modified Friedel-Crafts reaction (13). The first step involves the reaction of excess dimethylaniline with phosgene:



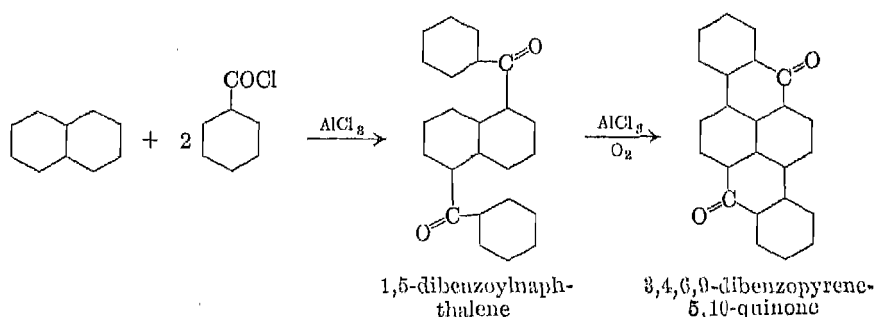


Without isolating the intermediate, zinc chloride is added and the reaction proceeds:



The excess dimethylaniline over the four moles required (two moles as hydrochloric acid acceptors) is later recovered.

An interesting double use of Friedel-Crafts syntheses is in the formation of a yellow vat dye, dibenzopyrenequinone (2). The first step is a typical acylation, and the second step using aluminum chloride and oxygen is an example of ring closure involving loss of hydrogen:



The manufacturing process, of German origin, is outlined below because equipment and conditions are typical of many of the Friedel-Crafts reactions used in the U.S. Both steps may be run without isolation of the intermediate, dibenzoylnaphthalene. In the first step, 925 kg. of anhydrous aluminum chloride is added in  $\frac{1}{2}$  hour to 625 kg. of benzoyl chloride in a 2000-liter enameled kettle, the temperature rising to 80–90°C. (due to formation of the addition compound). After cooling to 63°, 200 kg. of naphthalene is added at 70° during 1 hour with agitation and the reaction is kept at 70° for 8 hours to complete the first reaction. This molten mass is then run during  $\frac{3}{4}$  hour into a 3000-liter enameled kettle containing 1100 kg. of anhydrous aluminum chloride and 210 kg. of sodium chloride melted at 130°. Oxygen is introduced at a rate of 60

cu.m. per hour, the temperature being raised to 160–170°, where it is held for 4–4.5 hours while 900 kg. more of aluminum chloride is added. The melt is then run into 10 cu.m. of water in a 16-cu.m. tank and further decomposed by the addition of hydrochloric acid. The product is filtered and dried. The yield of dye is 275 kg. (53% of theory). It is later subjected to purification by vatting, filtration, and oxidation with sodium hypochlorite.

Another unusual process used in Germany (42) involves the reaction of ethylene oxide with benzene in the presence of aluminum chloride to produce  $\beta$ -phenylethyl alcohol, a perfume constituent (see Vol. 2, p. 487).

Aluminum chloride has been found valuable in the condensation of phosphorus oxychloride and phenols to make triaryl phosphates, which are used as plasticizers (43).

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G. W. PEDLOW AND P. E. HOCH

**FRIEDELIN**,  $C_{30}H_{50}O$ . See *Cork*, Vol. 4, p. 482.

**FROZEN FOOD**. See *Food and food processing*.

**FRUCTOSE**,  $CH_2OHCO(CHOH)_3CH_2OH$ . See *Carbohydrates*, Vol. 2, pp. 870-71; *Sugars*.

**FRUITS**. See *Food and food processing*; *Food analysis*.

**FUCHSIN(E)**,  $[(NH_2C_6H_4)_2C:C_6H_3(CH_3):NH_2]Cl$ . See *Triphenylmethane dyes*.

**FUEL OIL**. See *Petroleum*.

## FUELS

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See also *Carbonization*; *Coal*; *Fuels, synthetic liquid*; *Gas, manufactured*; *Gas, natural*; *Gasoline*; *Lignite*; *Peat*; *Petroleum*; *Rocket propellants*; *Shale oil*; *Tar and pitch*; *Wood*.

## SURVEY

Any source of heat energy may be classed as a fuel. Coal, petroleum, and natural gas are the most important fuels. In these, the potential energy is in the form of carbon or hydrocarbons which are burned, usually with oxygen from the air, to release the energy. However, electric energy, when used as a source of heat, may also be classed as a fuel. Although, for the most part, electrical energy is generated by conversion of heat energy from one of the carbonaceous fuels, an important source is hydropower. Also in chemical and metallurgical processes, the heat of reaction in certain steps is often usefully employed. Examples are the combustion of sulfur compounds, pyritic smelting, and the combustion of manganese, silicon, and phosphorus in the Bessemer process for making of steel.

For rockets for scientific and military uses, various chemical compounds which release energy at a high rate, such as alcohol, ammonia, and hydrazine, are used as

fuels. Nuclear energy may also soon be a source of heat for industry, and fissionable materials will then have to be considered as fuel (see *Nucleonics*). For the purpose of this discussion, however, only coal, petroleum, natural gas, wood, and electricity will be considered as fuels. See also *Furnaces*; *Power generation*.

### Natural and Processed Fuels

Wood is normally marketed without processing, except for cutting to size. A considerable amount is carbonized, however, to make charcoal for various fuel uses.

Coal also is mostly used as such, although the equipment and plants for sizing, for reduction of ash, and for treatment to reduce dustiness are truly processing plants. An important processed fuel made from bituminous coal is coke. In the process of carbonization, tar and gas are produced which are likewise used for fuel purposes. Producer gas is made from coal or coke by blowing with air and steam. Water gas is made by alternately blowing the fuel bed with air and steam, or by substituting oxygen for the air in a gas producer. The main combustible gases produced by these processes are hydrogen and carbon monoxide; hence, the calorific value of water gas containing the normal amount of inert gases seldom exceeds 300 B.t.u. per cubic foot. By the use of oxygen and steam at high pressures, a gas of higher calorific value, 450–475 B.t.u. per cubic foot, may be made. Such a gas is suitable for city distribution where the standards do not call for higher calorific values.

By synthesis from carbon monoxide and hydrogen made from coal, or by reacting coal with hydrogen at high pressures, liquid fuel can be made. Although technically possible, large-scale industrial plants will not be built until dictated by the state of supply of natural petroleum, the relative costs of this and the synthetic product, or by a state of national emergency.

Petroleum can be used for fuel as produced as crude oil, but it is more economical to separate it into fractions ranging from gasoline to heavy residual oil by distillation. In certain refining processes, a residual petroleum coke is made. This serves as a desirable low-ash fuel for many purposes, but it is more advantageously used as a source of industrial carbon.

In addition to the liquid and solid products, gaseous fuel (propane and butane) is made in the refining process. These are distributed under pressure as LP (liquid petroleum) gas. By reaction with steam at high temperatures in several somewhat different processes, fuel gas of medium to high calorific value, 500–1000 B.t.u. per cubic foot, is made for city use. Oil is also thermally cracked in the regenerators of water-gas sets to increase the calorific value of water gas to a point where it can be used for city distribution.

A probable future source of petroleum, when proper economic conditions prevail, is oil shale, from which a heavy crude oil can be extracted by distillation.

Natural gas is a fuel that is principally used as produced, although sulfur compounds and natural gasoline are removed when necessary. By pipe line, the gas is transmitted up to 2000 miles from the wells for industrial and residential uses. To supplement the supply of manufactured gas without a change in characteristics or calorific value, natural gas is often "re-formed" by a process of partial oxidation, or by a catalytic cracking in the presence of steam in continuous or intermittent reactors.

Hydrogen and carbon monoxide for the synthesis of petroleum may be produced from natural gas by controlled oxidation or by catalytic cracking in the presence of steam.

This brief description of a number of processes shows the possible convertibility of the various forms of fuel into the other forms when the requirements and economic conditions demand and permit the conversion.

### Criteria for Selection of Fuel

The criteria that dictate the selection of a given type of fuel for any use are:

- (1) Suitability to process.
- (2) Supply—availability and reliability.
- (3) Cost—under this heading may be considered:
  - (a) Cost per unit of heat value.
  - (b) Efficiency of utilization.
  - (c) Cost of equipment.
  - (d) Maintenance of equipment.
  - (e) Labor and convenience.
  - (f) Fuel and refuse handling.
  - (g) Auxiliary power.
- (4) Cleanliness.

### SUITABILITY

The first requirement of a fuel is, obviously, that it be suitable for the process to be carried out. For many purposes, any type of fuel can be used; for others, one type of fuel is uniquely suited. For example, steam can be generated in boilers fired by solid, liquid, or gaseous fuel, and even by electrical energy with proper equipment. For the smelting of iron from its ores or for foundry fuel, however, a solid fuel of particular characteristics is required; coke generally made from bituminous coal has been and will probably continue to be pre-eminently suitable although both charcoal and anthracite have been used. Coke may be made by charging only one bituminous coal to the oven, but usually the charge consists of a blend of a high-volatile and a low-volatile coal. Some anthracite may be substituted for low-volatile bituminous coal.

Under certain conditions, the requirements of quality of the product are the predominant factor in the choice of the fuel and will outweigh other considerations of cost and ready availability. The chemical, ceramic, and metallurgical industries furnish such examples.

For the generation of steam or the heating of air for power or for comfort heating, coal, oil, or gas is suitable when used in the proper equipment. Generally speaking, there will be no difference in the quality of the steam or of the warm air ascribable to the quality of the fuel.

Coal is often cited as preferable to oil or gas for comfort heating because of the fact that a fuel bed is always present in the furnace or boiler to liberate heat even when the thermostat is not asking for heat. In contrast, with oil or gas no heat is liberated after the thermostat is satisfied, and, as a result, a stratification of air in the space to be heated may occur before the thermostat again calls for heat. This leads to an unpleasant, chilly condition called "cold 70." This condition is, it is true, more common with oil or gas than with coal, but it can be corrected with the former fuels by the proper type of thermostatic controls. The fact that coal continues to liberate heat from the bed in the "off" period is not totally without its disadvantages as it frequently leads to "overshooting" of the thermostatic temperature, particularly in mild weather.

## SUPPLY—AVAILABILITY AND RELIABILITY

Table I summarizes the reserves of coal, oil, and natural gas of the United States.

TABLE I. Reserves of Coal, Oil, and Natural Gas in the U.S.

Material	Reserve
Coal, million tons <sup>a</sup>	
Anthracite.....	15,400
Bituminous.....	1,407,800
Subbituminous.....	818,100
Lignite.....	939,500
Total equivalent bituminous <sup>b</sup> .....	2,559,100
Petroleum, million bbl. <sup>c</sup>	
Crude oil.....	24,649
Natural gasoline.....	3,729
Oil shale <sup>d</sup> .....	92,000
Natural gas, million cu.ft. <sup>e</sup> .....	180,381,344

<sup>a</sup> See reference (4).

<sup>b</sup> All types of coal calculated to basis of bituminous of heat value of 13,100 B.t.u. per pound.

<sup>c</sup> See reference (1).

<sup>d</sup> See reference (7).

The reserves of coal and their distribution by states are discussed in detail in the article on *Coal*. As mentioned there, doubt has been recently expressed concerning the accuracy of the estimates of the reserves of coal, and some estimate that the economically recoverable reserves may be no more than one-half of the values quoted. New surveys for more accurate estimates will probably be authorized. Coal is widely distributed in the U.S., but practically all of the anthracite is found in Pennsylvania, and the subbituminous coal and lignite, which constitute a large fraction of the reserves, are mainly found in Wyoming, North Dakota, Colorado, and Montana.

The values for the reserves of crude oil, natural gasoline, and natural gas are revised yearly by a Joint Committee of the American Petroleum Institute and the American Gas Association. They are called the proved reserves. The reserves estimated for the preceding year are revised upward or downward, as the change in pressure of the wells indicates, the new discoveries are added, and the production of the year is subtracted. Although the annual rate of production and use of petroleum has been of the order of one-twelfth of the proved reserves and of natural gas about one-thirtieth for several years, the extensions and new discoveries have about equaled the use. Hence, the ratio of reserves to annual production has not changed greatly in recent years despite a greatly increased use of both fuels.

The production of oil from shale is now only in an exploratory stage. The oil has quite different characteristics from crude oil from the earth. If the estimates of reserves are accurate, it is seen that they are almost four times the reserves of crude oil. Oil shale of greatest oil content is found principally in Colorado. The principal reserve of crude oil is in Texas which had 54% of the reserves as of January 1, 1950. The four states Texas, California, Louisiana, and Oklahoma had 82% of the reserves.

Of the total reserves of natural gas, Texas had 55%, and Texas, Louisiana, Kansas, and Oklahoma had 84%.

On a heat-value basis, coal accounts for almost 99% of the total fuel reserves as listed in Table I. Even if the estimates of coal should be revised to one-half of the values given, coal still remains the basic fuel of the U.S.

The reserves of fuels elsewhere in the world are less accurately known than are those of the U.S. Fieldner estimates that the U.S. reserves amount to 45-50% of the world reserves of coal (2). In 1946, the total proved reserves of oil were estimated by Standard Oil Company of New Jersey to be 59 billion barrels (6). The largest reserves known outside of the U.S. are in Iran and Iraq. These fields are being rapidly developed, and oil from the fields is now being imported into the U.S. Little is known of the reserves of natural gas outside of the U.S.

**Reliability** of supply is vital for any application of heat energy and must be considered both from the long-range and short-range viewpoint. Factors likely to affect the reliability of supply are the life of the reserves, international politics or wars, labor difficulties, and weather disturbances. The effects of war on the coastwise and ocean movement of oil in World War II need no recounting.

Because ample supplies of coal are available within the continental United States, the threat of failure of supply of coal lies only in manpower and equipment shortages, and in overtaxed transportation facilities in time of war. During the war, these often disturbed but never disrupted the supplies of coal. Labor difficulties have, at a number of times in recent years, stopped the production of coal long enough to cause serious difficulty to industry and the public from shortage in fuel supply. The oil and natural gas industries have not been completely without difficulty, but their experience has had much less acute repercussions.

Weather conditions often disturb the mining and transportation of coal; floods may cause failure of oil and gas lines; and snow, sleet, and wind frequently cause failures in electrical transmission lines. Such stoppages are not usually of long duration, and the effect of stoppages of this and other types must be considered in the light of possible storage of supply.

Both coal and oil can be stored in amounts limited only by the ground space available, but oil has the advantage that it undergoes no deterioration in storage, whereas some coals change to some degree. Subbituminous coals and lignites "slack" or break up if stored in the open because of the gradual loss of their content of water, and are subject to spontaneous ignition. By underwater storage or other specially devised methods, this slacking and spontaneous ignition may be prevented. No tanks are required for coal as they are for oil, but proper facilities for packing to avoid spontaneous heating and for ease in reclaiming are necessary. Oil has the advantage of ease of placing in storage and removal.

Gas can be stored, but only in limited amounts, usually but a few hours' supply, and, for practical purposes, electricity cannot be stored at all. Where rock structures permit, natural gas is sometimes stored cheaply in underground reservoirs. The history of continuity of service by gas is most excellent, and the continuity of service on electric transmission lines has steadily improved.

#### COST

The cost of a fuel is usually a most important factor in its selection, although adaptability and availability are criteria which must be given first consideration. For residential comfort heating, the importance of the cost will depend on the income of the user. To those of low income, cost is all-important and, shortsightedly, some will consider only cost of coal per ton or oil per gallon with no thought of the heating value. In industrial applications, the importance of cost will depend both on the amounts used and on the percentage of total cost of the product represented by fuel.

**Cost per Unit of Heat Value.** Figure 1 presents a series of nomograms from which the cost of heat in dollars per million B.t.u. in the fuel can be readily obtained. To use the nomographs, a straight edge is laid through the calorific value of the fuel and the cost of the fuel; the cost of heat per million B.t.u. is read at the intersection with the central scale. Typical lines are drawn on the chart for illustration.

For example, oil of 138,500 B.t.u. per gallon that costs 8.5 cents per gallon gives a fuel cost of 62 cents per million B.t.u.; coal of 13,000 B.t.u. per pound that costs \$14.00 per ton gives a cost of 55 cents per million B.t.u.; electricity that costs 0.5 cent per kilowatt-hour for which the heat equivalent is 3,412 B.t.u. gives a cost of \$1.47 per million B.t.u.; and similarly for wood and for gas. To obtain the cost of fuel energy as utilized, divide by the per cent efficiency of utilization and multiply by 100. Thus if the efficiency is only 50%, the cost is doubled.

**Efficiency of Utilization.** The efficiency with which a given fuel will be utilized depends to a considerable degree on the equipment in which it is used, the workmanship of the installation, and the skill in adjustment, maintenance, and operation. Hence, there is often a greater range of variation in the efficiency of one fuel among various installations than among different types of fuel in similar installations. There are, however, certain general distinctions among fuels which usually characterize their efficiency of utilization. These will be discussed principally from the viewpoint of the use of the fuels in steam generation for power and for comfort heating.

*Coal.* With the latest engineering designs of large industrial and commercial boilers which are well instrumented, well operated, and include heat-recovery equipment such as air heaters, efficiencies of up to 90% can be obtained and maintained in day-to-day operation. The losses in heat in the flue gas are cut to a minimum by low exit temperatures and low excess air, and losses in unburned combustibles in the flue gases and in unburned solid combustible in the ashes are maintained at almost negligible quantities. Such operation can be maintained even with low-rank and low-grade subbituminous coals. The loss in heat inherent in this type of coal, because of its high moisture content, is minimized by efficient heat recovery.

Although the loss in the heat required to evaporate the moisture from coal and to superheat the resultant steam to the flue-gas temperature increases in direct proportion to the moisture content and in inverse proportion to the calorific value of the coal, it is not a major loss with any coal. For example, a bituminous coal which contains 4% moisture and has a calorific value of 13,000 B.t.u. per pound when fired will have a loss due to the moisture content of approximately 0.4% if the flue-gas temperature is 600°F. A subbituminous coal which contains 24% moisture and has a calorific value of 9,000 B.t.u. per pound will have a loss due to the moisture of about 3.4% at the same flue-gas temperature of 600°F. Thus, the difference in the percentage loss in efficiency because of moisture will be a determining factor only in those installations which are operated at the peak of efficiency.

A source of loss of heat greater than that due to the moisture in the coal is that caused by the water formed from the combustion of the hydrogen of the coal. As the hydrogen contents of coals do not vary widely, the loss of heat per pound of coal will not vary greatly among coals, but the percentage loss will vary inversely as the calorific value of the coal. If the bituminous coal cited above has a hydrogen content of 5%, the loss because of moisture formation will be about 500 B.t.u. per pound of coal. If the subbituminous coal has a hydrogen content of 6%, the loss will be about 700 B.t.u.



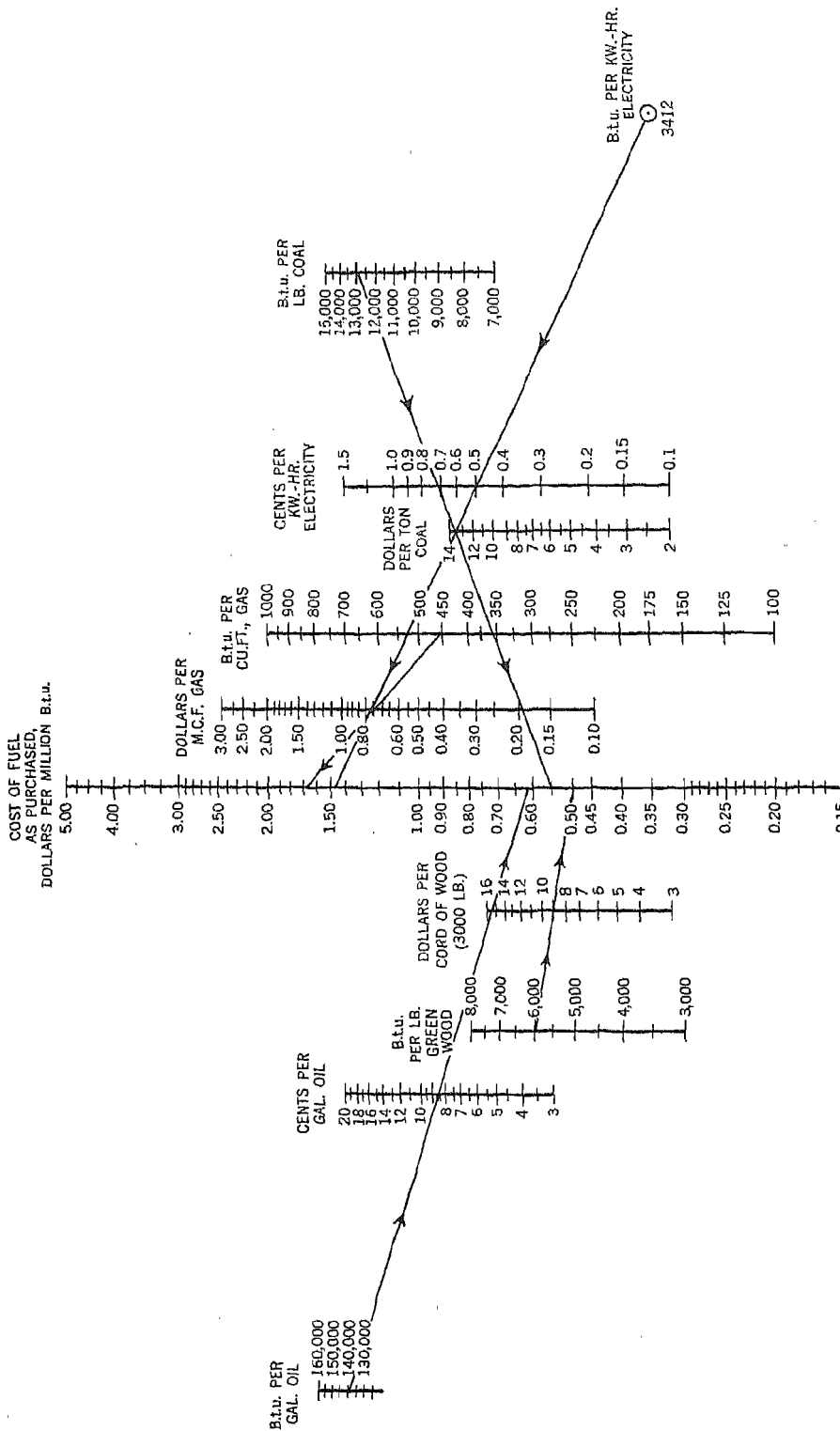


Fig. 1. Nomographs for calculation of cost of heat energy in various fuels.

per pound. But, because of the difference in calorific value of the coals, the percentage losses will be about 4.5 and 7.7%, respectively, for the bituminous and subbituminous coals.

Smaller power boilers, such as are used in commercial and small industrial plants, usually have mechanical stokers, but have less extensive heat-absorbing surface, are less well instrumented, and have less well-trained operating personnel. As a consequence, the losses in the flue gases are higher because of higher excess of air and higher temperatures, and the loss in carbon in the ash and refuse may be appreciable. Such plants, because of improper attention, often produce excessive smoke. In itself, the smoke is not usually a source of heat loss, but it indicates the possibility of the presence of such unburned combustibles as carbon monoxide and hydrocarbons. Efficiencies of 80% are possible in the best of such small plants, but 70–75% are more usual; with poor practice, they may fall to 60–65%.

*Coke*, the solid residue from the carbonization of bituminous coal or from the distillation of petroleum, varies widely in its characteristics according to the method of production. The primary use of high-temperature coke, that is, that carbonized at about 1800°F. in coke ovens, is as a metallurgical fuel for the iron blast furnace or foundry cupola, although it is also an excellent domestic fuel. Its volatile content is usually 2% or less. Low-temperature coke, carbonized at temperatures of 900–1000°F., is characterized by a volatile content of 10–18% and a greater ease of ignition and a higher reactivity than high-temperature coke. Because all of the ash in the coal must remain in the coke, the ash content of coke is always higher than that of the coal from which it is made, by about 40% or more. The moisture, however, is driven off. As a net result, the calorific value of the product of the carbonization of high-moisture coals, such as subbituminous coals, can be higher than that of the coal carbonized.

*Wood*. Characteristics of wood, from the fuel standpoint, are the high hydrogen content and, as usually fired, the high moisture content. The result is that, despite the fact that it can be burned in properly designed and operated equipment with low excess air and a low dry-flue-gas loss, the loss of heat in water vapor in the flue gas will be high. The reactivities of wood and the charcoal produced in burning are high, and the loss in unburned carbon in the ash should normally be very low. The efficiency of large boilers in which hogged fuel is burned will be in the range of 65% and that of smaller equipment will range downward from this value dependent on the percentage of excess air maintained and the area of heat-absorbing surface provided. This statement applies to equipment as small as residential heating equipment using sawdust burners.

*Oil*. As oil is practically 100% volatile, by proper volatilization or atomization, better mixing with the air can ordinarily be obtained than with coal. Hence, higher rates of burning in a given volume with lower excess air should be possible with oil than with coal. In larger equipment, with proper attention to atomizing nozzles and to the rate of air supply, efficiencies can be maintained at a high level, but not appreciably higher than in a well-operated, coal-burning plant.

Oil contains more hydrogen than coal, and, as the heat of vaporization of the water formed from burning the hydrogen is lost with any fuel, this loss will be greater than with coal. The difference is not large; it will ordinarily be 2–5% greater than with coal. This is just about the extent of the loss from the evaporation of the moisture content of a high-moisture subbituminous coal.

Smoke should not be a problem with oil, but, with improper mixing or with too

low an excess of air, smoke may be very serious. Care must be exercised that, to avoid smoke, the excess air is not so greatly increased as to result in excessive losses in sensible heat.

**Gas.** Natural gas is usually the only gas available at a cost low enough for use in industrial boilers, but both natural and manufactured gas are used in metallurgical, chemical, and ceramic processes and in residential heating. Of the three types of fuel, gas is the most readily mixed with air, and, for industrial applications, complete pre-mixing of the air and gas is often used. Low excesses of air, often approaching the theoretical, are frequently maintained.

The content of hydrogen in either natural or manufactured gas is even higher than in oil, and the loss in heat of vaporization, other conditions being equal, is 4–5% higher than with oil and 6–8% higher than with coal. The water-vapor content of the flue gases is so high, that care must be exercised to prevent such a low flue-gas temperature that condensation will occur, especially if there are any sulfur compounds in the gas, for condensation leads to corrosion of metals of the equipment.

Because gas burners do not usually have mechanically driven parts subject to wear and improper adjustment, the efficiencies, once set, are likely to be maintained at that level.

**Electricity.** The cost of heat in the form of electricity is, at rates that usually obtain, the highest for any source, but, inasmuch as there is no loss in unused fuel or in sensible or latent heat in products of combustion, the efficiency of utilization can be practically 100%. In fact, by means of the "reversed-refrigeration" or "heat-pump" principle in which heat is pumped up from a low to a high level, if the source of heat is ground water, an over-all thermal efficiency of 250–400% can be obtained. The efficiency obtained increases as the temperature of the water used as a source of heat increases.

Electric energy cannot be stored to provide insurance against interruption of service except by expensive conversion to direct current and the use of storage batteries, but, by conversion to heat, it can be stored. This principle has had extensive use in water-heating service when electric power is used to heat water in "off-peak" hours and the hot water is used through the day. By the use of water in pressure vessels or by the use of refractory materials, heat can be stored for comfort heating.

**Cost of Equipment.** No attempt is made here to present a comprehensive analysis of the relative cost of equipment for the utilization of various fuels. It is only desired to call attention to the fact that it should not be neglected in any analysis of the cost of fuel.

The cost of the equipment for burning the different fuels for industrial purposes is usually not so greatly different as to be a determining factor in the selection of a fuel if there is a substantial difference in the cost of heat utilized. If the costs of various available fuels are similar, then other factors such as labor costs will usually be governing.

The required capacity of fans for the supply of air for the burning of fuels does not vary for different fuels except in so far as the efficiency of utilization of the fuel affects the amount of fuel burned. This results from the fact that the amount of air required for the liberation of a given amount of heat is essentially a constant, independent of the type of fuel burned.

A current trend for large boilers in many parts of the country where oil, coal, and natural gas may be available is to install equipment in which any one of the three can

be used, dependent upon the cost. As the cost of a fuel changes or it becomes unavailable for any reason, the change is readily made to another fuel. Burners are available in which pulverized coal, oil, or gas can be burned with little change.

**Maintenance of Equipment.** The cost of maintenance of the fuel storage, handling, and burning equipment is definitely a part of the fuel cost and must be considered. It will ordinarily be found in larger power plants that this cost is higher for coal-fired equipment than for the other fuels because of the wear of the coal and ash conveying equipment, the wear of pulverizers, or burning of iron in stokers. Water-cooling of furnaces has largely eliminated the problem of the failure of refractories, but, if there are refractories, they may fail in oil- and gas-fired furnaces as well as those fired by wood and coal. The order of difficulty will depend on the type of ash in the coal or wood.

**Labor and Convenience.** With oil and gas burning, the attention to the movement of coal and ash is definitely eliminated, and savings in manpower can result in large plants. In small plants, savings in manpower may not be possible because, by state laws, licensed operators must be present whether they are occupied in removal of ashes or are idle. In residential heating equipment, the elimination of labor is usually the most important factor deciding the adoption of oil or gas. This is not from the viewpoint of saving in cost, as most commonly the labor is done by some member of the family and is not charged in money against the cost of heating; saving in labor is, in this case, a matter of convenience. Of the sources of energy, oil, gas, and electricity, the latter two are the most convenient because even the need to order a supply is eliminated and payment is made after the energy is used.

**Fuel and Refuse Handling.** The necessity to handle ash and refuse adds to the cost of equipment and to the cost of labor when burning coal as compared to gas and oil, and could have been discussed under those headings, but is placed separately for emphasis. Careful analysis of this factor is required when a selection is to be made among several coals of varying ash content. For large plants, credit must be given to coal for the sale value of the ash and cinder for which, in some areas, a substantial demand exists for cinder block, driveways, and fills.

**Auxiliary Power.** The auxiliary power for conveying coal, pumping oil, supplying air or steam for atomization of oil, supplying air for combustion, and for conveying ash and refuse are substantial additions to the cost of fuel. Since gas is normally supplied under pressure, and because the pressure against which the air must be supplied is not high, the auxiliary power requirements for gas are lower than those for coal or oil. The power requirements for pulverized coal are in the range of 20–30 kilowatt-hours per ton (for pulverization and air supply) and are 10–20% above those for underfeed stokers. The power requirements of spreader stokers are lower than those of underfeed stokers because of the lower pressure at which the air for combustion is supplied.

#### CLEANLINESS

The cleanliness with which a fuel may be burned is often a most important factor, not only in residential heating, but also in industrial use because of the increasing civic consciousness that dirty air is detrimental to a community. Coal can be a dusty, dirty fuel to handle, but the treatment of coal with small amounts of oil can practically eliminate this dust nuisance. Care in wetting down ashes can largely remove dust in their handling. Smoke is practically unnecessary in burning coal in both large and small stokers of modern design and also in burning pulverized coal. For pulverized

coal and spreader stokers, fly-ash collectors, to eliminate emission of objectionable dust from the stack, are available and should be installed. For existing plants where a smoky stack is common because of faulty design of equipment, overfire air jets are available to eliminate the nuisance. A smoky stack with gas is almost an impossibility, but oil, with faulty operation, can give most objectionable smoke.

### Fuel for Railroad Locomotives

For the U.S. as a whole, the steam locomotive is still the leading motive power of the railroads. Within the last thirty years, oil has replaced coal on the steam locomotive in the West and Southwest where oil is more readily available and lower in cost than coal. Electric locomotives have had a relatively limited application in regions of very dense traffic, or where a combination of heavy grades and low-cost power has made their use favorable.

In the last twenty years, the Diesel-electric locomotive has rapidly come to the fore. The overall thermal efficiency of the Diesel is about 24% whereas that of the coal-fired steam locomotive is but about 6%. Thus, even where the cost of heat in coal is as little as one-third of that in oil, the fuel cost is lower with the Diesel. The first cost of the Diesel is greater than that of the coal-fired locomotive for the same horsepower output, but the outage for servicing the Diesel is less than that of the average steam locomotive, and more miles per month can be obtained with the Diesel. The cost of lubricating oil is higher for the Diesel than for the steam locomotive, but maintenance costs of Diesel locomotives have up to this time been favorable. Final judgment on maintenance will have to be reserved until comparisons can be made between Diesel and steam locomotives of similar age. It must be remembered that when comparisons are made on averages, Diesels of but a few years of service are compared with steam locomotives, many of which have been in service for 20-30 years.

A new development in railroad motive power that promises to be of much significance is the gas-turbine-driven locomotive. The Swiss Federal Railways has had an oil-fired gas-turbine locomotive for several years, and one was put on the rails in the U.S. in 1949. This unit has an efficiency little less than that of the Diesel, has no reciprocating parts, has no lubrication problems, requires no water, should cost less per horsepower, and uses heavy fuel oil of lower cost and higher calorific value than the Diesel.

An intensive program of research to adapt coal to the gas-turbine locomotive is now under way, both by the use of pulverized coal and by the gas producer.

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## COMBUSTION OF SOLID FUELS

The establishment of general principles that are of importance in practical application of the combustion of solid fuels has been based most successfully on properly conducted laboratory experiments under conditions permitting the control and independent variation of the variables affecting combustion rate but still approximating as closely as possible the general conditions found in the applications. To this refined form of empiricism, rather than to the many attempts made to relate burning to reaction rate from the physicochemistry point of view, is due most of the progress made in the rational interpretation of combustion applications.

Because combustion reactions are essentially chemical reactions, many attempts have been made to apply the concepts of equilibrium and of rate of reaction to them. Such attempts, by and large, have not been successful because (1) times are too short, usually, to reach equilibrium, and (2) temperatures are too variable from point to point to allow averaging or choice of a suitable value for the reaction constant. Use of the Arrhenius equation for reaction-velocity constants is not applicable for the study of the effect of temperature on rate of reaction. Furthermore, attempts at the measurement of reaction-velocity constants for solid fuels by many experimenters have led to no generally recognized and accepted method and to little agreement between results (5).

The difficulty of obtaining basic reaction-rate data in the combustion of solid fuels indicates very strongly that diffusion or mass-transfer rates, rather than reaction rates, are the limiting process. Thus, the establishment of relations governing rates of burning attainable must depend primarily on empirical solutions established in the laboratory under conditions simulating those found in the art. In short, there is no general theory of combustion, but there are many successful methods of burning subject to varying degrees of analysis. Some of the relations established for these methods are summarized in the next sections.

### Fuel Beds

The fuel bed represents a common form of burning solid fuels. Most solid fuels cannot be burned as solitary pieces when exposed to radiation losses on all sides, because their temperature will be so lowered that ignition is lost. The several pieces of fuel forming a fuel bed shield each other from these radiation losses and thus make it possible to maintain ignition under widely different conditions of operation. Fuel beds of various kinds have been devised to meet, in addition, a wide variety of fuel characteristics that will now be discussed.

### Fuel Characteristics Affecting Fuel Beds

**Caking.** From the point of view of their behavior when heated, all solid fuels can be divided into two groups (not sharply divided): (1) those that remain free-burning, and (2) those of the opposite kind that form a tarry cake in which the individuality of neighboring pieces is lost by their fusion into a sticky medium. This differentiation makes it apparent that, whereas the feeding to a fuel bed of a free-burning fuel may not interfere perceptibly with the distribution of the flow of air, the firing of a caking fuel, when matting is allowed to take place, will result in the establishment of channels of preferential flow of air at the boundaries of the matted regions, and control of the rate of

burning will be uncertain. In principle, maintenance of oxidizing conditions, around each of the pieces of fuel, as tar exudes from them, is the most effective way of minimizing caking; otherwise, mechanical action needs to be applied when the consistency of the cake is at the proper stage.

**Release of Volatile Matter.** All natural and some processed solid fuels release, when heated, gaseous products composed of water vapor, hydrocarbons, and hydrogen, and sometimes carbon monoxide and carbon dioxide. Some of these may evolve from the tars formed, but tar-free fuels also yield gases. The residual fuel, after these volatile substances have been distilled, is termed coke, char, charcoal, or simply residue. Cokes and chars vary greatly in their reactivity toward atmospheric oxygen, particularly when low-temperature combustion processes are involved. The term reactivity is rather loosely defined as it combines the concepts of ignition and of reaction rate. The reactivity of a fuel defines a temperature such that once it has been reached under adiabatic conditions, combustion can proceed at a continuous or accelerated rate, and reactivity also defines the rate of reaction obtained. No standard method is accepted for the determination of reactivity because the test conditions cannot be defined accurately, nor can the measure of reactivity obtained be related to them. However, differences in reactivity are of consequence only in some types of fuel beds. A simple example is the open grate, as used in fireplaces, where ignition can be easily lost. The reactivity of cokes produced under a given heating schedule appears to correlate well with the volatile-matter content of the coal from which they are formed (12). The reactivity of cokes in their reaction with carbon dioxide to form carbon monoxide, which is to be differentiated from reactivity toward oxygen, is important primarily in small gas producers, as may be used in connection with motor vehicles, because the high surface-volume ratio causes high external losses of heat and thus lower internal temperatures.

The release of combustible gases from solid fuels presents the advantage that with proper design of the furnace a long flame with good radiation properties may be obtained to transfer heat for the heating of certain materials. The admission of secondary air to burn the gases is relatively simple in such reverberatory furnaces. However, in boiler furnaces the burning of the combustible gases leaving the fuel bed is not obtained by simple means because, owing to laminar flow due to low velocities, lack of furnace volume, and rapid cooling of the products of combustion, there is not enough turbulence or time for mixing with air and for completion of the reactions. In this instance, overfire air jets are required, which act through the establishment of turbulence where laminar flow would otherwise prevail (2). In plants of small capacity, the burning of the gases by overfire air jets does not usually add to the fuel economy but will prevent smoke emission; both objectives are met in the larger plants because the air-fuel ratio is apt to be under better control in these plants.

**Release of Ash.** The ash accompanying all solid fuels may, during the burning, so coat the pieces of residual fuel as to affect the rate of combination with the oxygen supplied, or may so fill the void spaces between the pieces of fuel as to restrict the flow of air greatly, or, at the high temperatures prevailing in fuel beds, may, by fusion and subsequent solidification in cooler regions, cause the formation of clinker that will affect the uniformity of flow of air. Elimination from the fuel bed of the ash released and control of its form are difficult problems of the art, since agitation may promote mixing to a composition of lower fusion temperature. If the ash has an appreciable content of iron oxides and these are allowed to be transported into a reduction zone of

the bed, severe clinkering may result because of the low melting point of the ferrous compounds formed. The deeper and larger beds are more conducive to clinkering because of the higher temperature of their oxidation zone and because of the presence of a reduction zone and its effect on the form of the ash.

**Release of Carbon Monoxide.** One of the most important actions occurring in fuel beds arises from the fact that carbon can form a monoxide and a dioxide. It is believed that both oxides can be released at the surface of burning coke, depending on its reactivity. Any carbon monoxide formed in the oxidation zone, where oxygen is available between pieces, is burned to carbon dioxide, whereas any carbon monoxide formed in the reduction zone, where carbon dioxide reacts with carbon, does not effectively react further within the bed. Consequently, as will be shown later, the composition of the gases in a fuel bed is a function of the thickness of the bed and of the amount of heat available for the endothermic reaction  $C + CO_2 \rightarrow 2CO$ . This heat must come from the exothermic reaction  $C + O_2 \rightarrow CO_2$  less heat losses to the surroundings. The formation of carbon monoxide in deep fuel beds is utilized in gas producers as a means of gasification for the production of combustible gas. In the thinner beds of boiler furnaces, the production of carbon monoxide adds another gas to the others released from the fuel and which must be burned above the bed.

**Fuel-Bed Homogeneity.** Although stable fuel beds have a static appearance, there is necessarily a flow of fuel pieces, accompanied by change in their size and weight as they are consumed. Control of this process to allow for enough lateral motion so that voids will not develop and the relative homogeneity of the bed will be maintained cannot be taken for granted, even when gravity is assisting. However, such control is required to insure effective contact of the oxygen supplied with the fuel. With most hand-fired fuel beds, maintenance of the homogeneity of the bed is one of the attributes of a good fireman; the various mechanical stokers must also perform this function.

### Elementary Types of Fuel Beds

Developments in the art of mechanical firing and in certain forms of domestic heating equipment have led to the use of fuel beds of different kinds to cope with the various fuel characteristics that have been discussed. These beds differ markedly in their properties and are best analyzed when divided into elementary types.

The elementary beds are defined in terms of the relative direction of flow of the air entering the burning zone to the direction in which the fuel enters the plane of ignition that marks one of the boundaries of the active fuel bed. The "plane of ignition" is the area where the fuel reaches its ignition temperature; it may be an irregular surface with convexities and concavities, but this surface can be considered as a plane without error. The plane of ignition is *real* if the temperature required for ignition is reached in the presence of free oxygen; it is *virtual* if the temperature of ignition is reached in the absence of oxygen. From this point of view, there are three types of elementary fuel beds: (1) the overfeed bed, (2) the underfeed bed, and (3) the cross-feed bed. These fuel-bed types and modifications of them, depending on whether ignition is restricted or unrestricted by control of the quantity of raw fuel present, are found singly or in combination in nearly all fuel beds in practical use.

#### THE OVERFEED BED

The overfeed bed is one for which the direction of the air entering the burning zone is parallel but *opposite* to the direction in which the fuel pieces enter the real or



virtual plane of ignition. This type of bed is exemplified (1) in conventional hand-fired furnaces where the fuel is burned on grates through which the air is passing, (2) in fuel beds mechanically fired by spreader stokers including the stoker-fired steam locomotive, and (3) in conventional gas producers and water-gas machines. In gas producers, devolatilization of the fuel takes place in the reducing atmosphere of the top of the generator; with spreader stokers, devolatilization of the finer sizes of fuel may be substantially completed while the fuel is in motion through the furnace before falling on the bed, but the larger pieces are devolatilized on top of the bed.

Figure 1 illustrates the general characteristics of the curves obtained when gas composition, observed temperatures, concentration of ash released, and relative volume

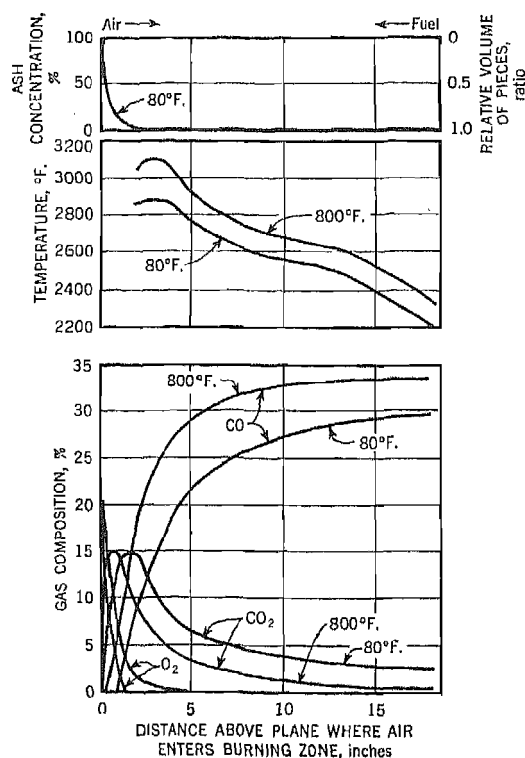


Fig. 1. Relations of gas composition, observed fuel-bed temperature, and ash concentration to thickness of overfeed bed, with combustion air at room temperature (80°F.) and preheated to 800°F. and high-temperature coke of size  $1\frac{1}{2} \times 1$  in. (11).

of piece are plotted against the thickness of the overfeed bed. Curves are given for air preheated to 800°F., and for air at 80°F. The percentages of nitrogen and of the water vapor or steam, that are always present, are not shown. With a sufficient thickness, the bed consists of two parts (separated by an indefinite boundary): (1) an oxidation zone where oxygen is consumed, carbon dioxide reaches a maximum, and carbon monoxide begins to appear, and (2) a reduction zone where the proportions of carbon dioxide and carbon monoxide approach an equilibrium value determined largely by the extent of heat losses to the surroundings and therefore by the extent of any air preheat.

The thickness of bed required for the complete disappearance of oxygen, and consequently the shape of the carbon dioxide and carbon monoxide curves, depends on the initial size of fuel pieces entering the ignition plane, as oxygen will be present for increasing thicknesses of bed as the size of piece is larger. It is emphasized that the relations of Figure 1 are for a relatively small size of fuel ( $1\frac{1}{2} \times 1$  in.). Control of the thickness of fuel bed thus makes it possible, in principle, to control the composition of the gases leaving the bed: (1) to obtain residual oxygen, which may be advantageous to destroy the caking properties of the fuel fired on top, or to burn the combustible gases released during devolatilization (although, in practice, caking generally occurs with the strongly caking coals and slicing of the cake by hand tools is required); (2) to obtain maximum carbon dioxide, which, however, results in the formation of an appreciable percentage of carbon monoxide; and (3) to obtain maximum carbon monoxide and minimum carbon dioxide for producer gas. A *real* plane of ignition obviously exists only with the thinner beds, for which not all the oxygen supplied is combined.

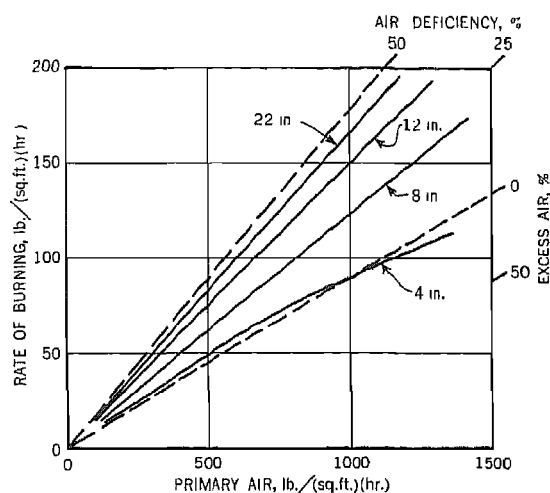


Fig. 2. Relation of rate of burning to rate of air supply for various thicknesses of overfeed beds, with high-temperature coke of size  $1\frac{1}{2} \times 1$  in. (10).

The shape of the ash-concentration curve shown in Figure 1 is slightly different for beds of different thicknesses in that the zero intercept must be at a point not above the level of the bed, but the curve is always characterized by a steep slope in the oxidation zone where most of the ash is released. The greatest change in volume of piece therefore takes place where oxygen enters the burning zone and this marks the level at which the fuel pieces vanish; the rate at which oxygen combines is also highest at this level. The exothermic effects obtained are more than ample to heat the air supplied to a temperature such that the rate of combustion can vary directly with the rate of air supply.

Figure 2 illustrates for the overfeed bed the interdependence of rate of burning, rate of air supply, and thickness of bed. The thickness of bed obtained results directly from the ratio of the rate of air supplied to the rate of fuel fired, so that the thickness for a given rate of air supply is greater as this air-fuel ratio is lower; for a bed maintained

at a constant thickness by suitable choice of the air-fuel ratio, the rate of burning increases directly with the rate of air supply. At high rates of air supply, a point is reached where the bed starts to "boil" and pieces are carried over with the gas stream; this occurs sooner with the thinner beds and results in a drop in burning rate shown diagrammatically by the curve for the 4-in. bed. Figure 2 applies to a high-temperature coke whose initial size of piece is  $1\frac{1}{2} \times 1$  in.; had the initial size of fuel piece been larger, the position of the lines for the various thicknesses of bed would have been rotated clockwise, and conversely for a smaller initial size of fuel. No rate of burning in the bed, for a given rate of air supply, can exceed the 50% air-deficiency line corresponding to the ultimate formation of carbon monoxide alone. The overfeed bed thus has the important characteristic that control of the rate of burning at a constant combustion efficiency is obtained directly by control of the rate of air supply. This method is the one used in all boiler-furnace installations with one notable exception: this is the steam locomotive, for which the rate of air supply is not independently controlled and does not normally increase with increase in rate of steam used because of the lowering of the gas-steam entrainment ratio, at the exhaust-steam nozzle, with increasing steam flow. In the locomotive, increase in the rate of burning over that obtainable by increase in the rate of air supply is obtained by increase in the thickness of bed; this process is not entirely satisfactory as the lowering of free oxygen in the gases above the bed adversely affects completion of the burning of the combustible gases released from the fines as they are projected into the firebox by the stoker, resulting in production of smoke. Use of overfire air jets in locomotives is not completely effective in preventing smoke, at high rates, because of the short time available for burning, the lower combustion efficiency of secondary as compared to primary burning, and interference with the distribution of fuel over the grate area. Although widely used in hand-fired domestic heating equipment, the overfeed bed is not well suited to this type of duty because intermittent firing results in initial deep beds that release, with all solid fuels, combustible gases difficult to burn, and with bituminous coals abundant smoke.

#### THE UNDERFEED BED

The underfeed bed is characterized by the fact that the direction of the air entering the burning zone is concurrent to that in which the fuel pieces enter the ignition plane; actually, both air and fuel enter the common boundary of ignition plane and burning zone together. Industrially, pure underfeed burning is found only during the first stage of burning in traveling-grate stokers. In these, at the fuel-feed end, ignition is at the top of the bed but travels downward against the flow of air from below until the grate is reached, whereupon the burning changes over to the overfeed type for the remainder of the travel to the ash discharge. Three kinds of behavior are possible, with reference to the rate of burning obtained during the underfeed burning phase, which depend on the rate of air flow. These are: (1) at low rates, when travel of the ignition plane against the flow of air will be so rapid that little burning of other than the distillation products will have taken place before ignition reaches the grate, (2) at higher air rates, when the rate of burning will rather rapidly become equal to the rate of ignition and an equilibrium burning bed of constant thickness will be maintained above the plane of ignition until ignition reaches the grate, and (3) at still higher rates, when ignition cannot advance against the air flow because the air and fuel cannot be heated rapidly enough and no burning takes place.

Figure 3 illustrates these different behaviors for a high-temperature coke of size

$1\frac{1}{2} \times 1$  in. At rates of air below 250 lb./sq.ft.) (hr.), the rate of ignition exceeds the rate of burning, and, although the latter increases directly with the air supply, a fuel bed of continuously increasing thickness is theoretically possible as long as there remains fuel to ignite against the flow of air. At low air rates, the rate of ignition increases with the air supply, but, with a greater rate of air supply, since more heat is needed to heat the air, less is available to bring the fuel to the ignition temperature, and thus the rate of ignition begins to decrease. Finally, at a rate of air supply of about 550 lb./sq.ft.) (hr.), ignition is lost and burning stops. Unlike the overfeed bed whose rate of burning increases directly with the rate of air supply, in the underfeed bed under equilibrium conditions, the rate of burning, generally speaking, decreases with increase in rate of air supply. Contrary also to the overfeed bed, for which the thickness of bed

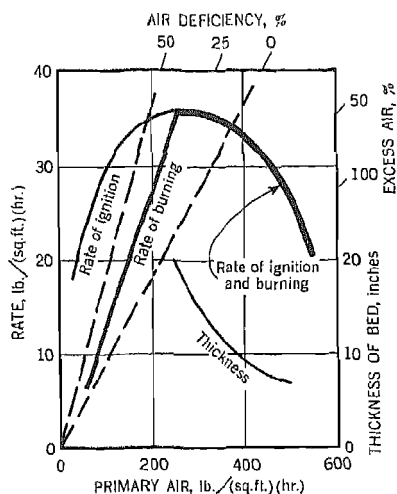


Fig. 3. Relations of rate of ignition, rate of burning, and thickness of equilibrium underfeed bed to rate of primary-air supply, with high-temperature coke of size  $1\frac{1}{2} \times 1$  in. (10).

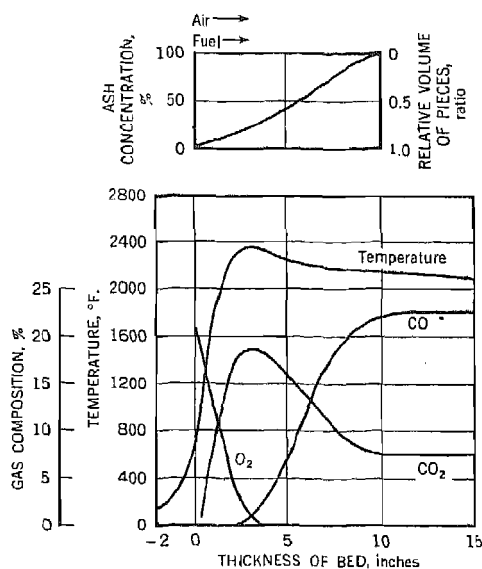


Fig. 4. Relations of gas composition, observed fuel-bed temperature, and ash concentration to thickness of underfeed bed, with high-temperature coke of size  $1\frac{1}{2} \times 1$  in. (11).

can remain constant at all air rates, in the equilibrium underfeed bed the thickness of bed decreases continuously with increase in air rate and so does the fuel-air ratio of the gases as shown by the increase in excess air.

Equilibrium beds covering lower ranges of rates of primary air supply than shown in Figure 3 can be obtained in pure underfeed burning by so restricting the rate of firing and, consequently, the rate of ignition, that an equilibrium bed will result; the thickness of fuel bed associated with such restricted ignition corresponds, however, to the thickness obtained in equilibrium beds under unrestricted ignition, for the same fuel-air ratio in the products of combustion. Modulation of the rate of burning, by means of the air supply, is obtained, however, only so long as the rate of air supply does not exceed that value which corresponds to the point where rate of ignition becomes the limitation.

Figure 4 shows the relation of gas composition of observed fuel-bed temperatures

and of concentration of ash released to the thickness of an equilibrium underfeed bed for a high-temperature coke of size  $1\frac{1}{2} \times 1$  in. From the foregoing, the characteristics of bed described in Figure 4 would obtain only at a specific rate of primary air supply. Hence, although the composition of the gas leaving the bed is of acceptable producer-gas quality, yet the impossibility of modulating the quantity of gas formed by modulation of the air supply rules out the underfeed principle for application to gas producers.

Comparison of Figure 4 with Figure 1 shows that for the same initial size of piece the extent of disappearance of oxygen and of formation of carbon dioxide and carbon monoxide are displaced substantially toward greater thickness of beds for the underfeed as compared to the overfeed bed. This displacement results primarily from the fact that since air and fuel enter together, the largest pieces are subject to the highest concentration of oxygen, whereas the opposite is true in overfeed combustion; the burning is thus more gradual and, as shown by the ash-concentration relation, rather uniform throughout the thickness of active bed. The consequence is that ash, as it is released from the fuel, is exposed to higher temperatures and to more strongly reducing conditions in the underfeed bed than in the overfeed bed, at similar burning rates; thus, clinkering is more severe and the use of steam to temper the fuel bed is not possible because of its adverse effect on ignition. This is another reason why underfeed burning is not suited to gas producers. This disadvantage is not apparent in traveling-grate stokers provided the rate of air supply is so adjusted that underfeed burning serves only to bring the ignition down to the grate level, without formation of an equilibrium bed, and overfeed burning is used to complete the burning.

Because underfeed ignition takes place in the presence of the atmospheric concentration of oxygen, conditions are well suited for such partial oxidation of the tars released from bituminous coals that caking will be destroyed or acceptably reduced. Application of this principle can be of great value to low-duty heating equipment such as space heaters and residual stokers; but completion of the burning by other means than underfeed burning is indicated (7).

#### THE CROSS-FEED BED

A cross-feed bed is one in which the direction in which the fuel pieces enter the plane of ignition is at right angles to the direction of flow of air. A burning process whereby the fuel bed is moved across the flow of air does not necessarily give a cross-feed bed if the plane of ignition is not parallel to the direction of air flow, for example, the traveling-grate stoker. The cross-feed bed is exemplified in the single or multiple-retort "underfeed" stoker, where underfeed refers to the method of introducing the fuel rather than to the burning principle used. There is not available for the cross-feed bed the type of laboratory information available for the other elementary beds regarding the relation of burning rate to rate of air supply and the relation of gas composition to thickness of bed. In fact, because the gradient of size of piece in the cross-feed bed is perpendicular to the direction of flow of air, the full range of sizes of pieces presents itself continuously to the air stream, which divides itself in a manner inversely proportional to the size of piece. Thus, the composition of the gases leaving the fuel bed depends on position, and averaging of composition requires weighting for intensity of flow. Control of rate of burning by control of rate of air supply is, however, obtained in burning equipment utilizing the cross-feed principle.

When so arranged that the motion of the fuel is generally horizontal, the cross-feed bed requires mechanical thrusts in order to advance and in order to fill with fuel pieces

the channels of preferential flow of air that constantly form in the general area where the larger pieces of fuel exist. Ignition of the incoming fuel is favored by the unequal flow of air, and some weakening of the caking properties of the fuel is obtained, so that the weakly caking fuels are particularly well suited to this type of burning. Strongly caking coals definitely require mechanical agitation to break the strong coke formed, and this agitation, as it is carried out in multiple-retort stokers, results in a lesser segregation of sizes. However, agitation results in the formation of stratified streams of gases, rich in unburned hydrocarbons, which will not mix with other streams in which excess air is present unless the furnace volume is very large or overfire jets are used to create turbulence. Agitation is also conducive to clinker formation, which in the single-retort stoker is considered beneficial, and in the multiple-retort stoker causes little difficulty.

The cross-feed principle of burning, when so disposed that the flow of fuel pieces is downward by gravity, makes it possible to provide true magazine feed without mechanical means, and a constant effective thickness of bed for constancy of fuel-air ratio over an extensive range of rates of air supply; however, the fuel so burned must be noncaking (7).

#### OTHER TYPES OF BURNING

Another elementary type of burning, for solid fuels, is **down-jet burning**, whereby a jet of air at rather high velocity is made to impinge on the fuel bed, the gaseous products of combustion also leaving the top of the bed, contiguously to the entering air, after making a "U" or an envelope turn within the bed. This type of burning, which is conducive to high burning rates and high combustion efficiency or low air-fuel ratios, has not received industrial application but is considered of potential importance (9).

A type of burning in fuel beds, which does not fall within the categories listed, is **surface burning** in the "cyclone" burner. A thin layer of fuel is held by incipient slag on the internal surface of the burner, which is in the shape of a volume of revolution, and the fuel is in contact with a stream of air rotating at high velocity (4). Small-size fuel and air are both admitted tangentially to the burner, but there is some question as to how much of the total fuel supplied burns in suspension and how much is held at the surface of the slag for surface burning. Proper design of the profile makes it possible to obtain high combustion efficiency and, more importantly, controlled slagging of the ash for ease of recovery and disposal.

**Periodic Fuel Beds.** Beds of solid fuels are used in periodic operation when it is desired to provide heat for an endothermic process by using the heat capacity of the bed to store heat generated by an exothermic process, such as combustion from an air blast, for use later in the cycle, for example, in the decomposition of steam by hot carbon. This is the basis of the water-gas process. A start has been made on a systematic investigation of the relation to capacity of thickness of bed, velocity of blast, duration of cycle, and size of fuel (3).

**Fluidized Fuel Bed.** Of growing experimental interest are beds of fuel maintained at the high rate of agitation required to give them a fluidized form, by passage through them of high-velocity gases, such as oxygen and steam, for the simultaneous production of carbon monoxide and hydrogen. Higher rates of mass transfer are possible by fluidization, but, in practice, there is a large carry-over of the smaller pieces resulting from the reaction (14), as well as a tendency for channeling (8).

## Burning of Solid Fuels in Suspension in Air

Although some of the fuel pieces fired by mechanical, pneumatic, or steam-jet-type spreader stokers are ignited while in suspension and may burn more or less completely before falling on the bed, this process cannot be considered a controlled one of burning in air suspension, whereas the burning of *pulverized coal* by standard methods is a controlled process. Little knowledge exists of the burning rates obtained in suspension burning from spreader stokers; it is known however, that the volatile matter released from rapid heating of the particles ignites first and the remaining coke burns last, if at all, while in suspension.

The burning of pulverized coal in air suspension is of great importance industrially, and primary data are available on this type of burning. The fundamental problem is to obtain the maximum, economical degree of completion of burning, by providing sufficient residence time or length of path in the furnace. The residence time required decreases with greater fineness of pulverization, with increased furnace temperature, and, within limits, with increase in excess air (13).

Figure 5 shows the relation of unburned carbon and of observed temperatures to residence time for three coals ground to the same fineness of 75-79% through 200

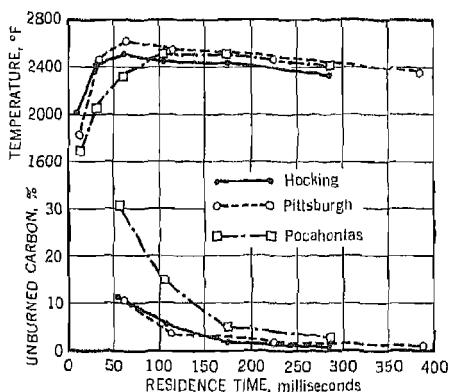


Fig. 5. Relation of unburned carbon and of observed temperatures to residence time, at an excess air of 20%, for a coal fineness of 75-79% through 200 mesh (13).

cause of weaker structure. The burning of anthracite in pulverized form is considerably hampered by its low volatile-matter content and its hard structure, which makes fine grinding costly.

The data shown were obtained by premixing all of the air with the coal before the burner. Industrially, such a process is too costly in power requirements for air handling and is circumvented by the use of turbulent burners that provide part premixing of the air with coal with further injection of air into the flame as burning proceeds. This method is advantageous for the maintenance of ignition over a wider range of fuel-burning rates from one burner.

Pulverized-coal burning offers good flexibility with regard to the form of ash produced, which is not affected as much by the temperature of the primary heat-transfer surface in the furnace as it is by size of furnace in relation to the rate of heat release (1). For the same total heat release, larger furnaces are required to give unshagged ash,

Of the three coals for which data are shown, Pittsburgh is a high-volatile, strongly caking coal; Hocking is a high-volatile, weakly caking coal; and Pocahontas is a low-volatile, strongly caking coal. Results obtained show that the rate of burning was independent of caking properties but decreased with decrease in volatile-matter content. The burning of coal in pulverized form thus represents an excellent method of obviating difficulties from caking. The lower burning rate obtained with low-volatile bituminous coal, due to difficulty in ignition, is corrected in practice by increasing the fineness of pulverization, which is greatly facilitated for these coals by the ease of grinding be-

and smaller furnaces for slagged ash, which may be tapped in liquid form. Entrainment of some ash by the gases is a problem in either case.

**Effect of Pressure on Burning of Pulverized Coal.** The burning of pulverized coal under pressure appears to be a possible means of supplying hot gases for the gas turbine. Investigation has shown that residence time required for a given completion of burning with low excess air is independent of pressure to several atmospheres or of air preheat to several hundred degrees (6). Rate of heat release can increase directly with pressure without shortening residence time, because velocity varies inversely with pressure and directly with firing rate, and the two variations compensate each other. These results suggest strongly that in this combustion process, as in all others involving solid fuels, the limitation is not rate of reaction but rate of mass diffusion of oxygen to the fuel. Operation at pressures higher than atmospheric has the important advantage, however, that the mass rate of firing can be increased, in a combustor of a given size, directly with the absolute pressure without decreasing residence time. Thus, the total rate of heat release, per unit volume of combustion space, may be increased directly with pressure.

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B. A. LANDRY

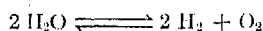
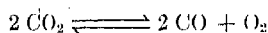
### COMBUSTION CALCULATIONS

For proper control of combustion processes and for design of combustion equipment, extensive application of the laws and techniques of thermodynamics is necessary. Before such an application can be made, material balances based on the law of combining weights have to be established. This use of the methods of stoichiometry (*q.v.*) and thermodynamics (*q.v.*) for evaluation of combustion processes is generally known as combustion calculations. By combining enthalpy balances with the material balances, most of the variables which are of interest can be determined directly and simply when the initial and final temperatures of the combustion reactants and products are known and when the existing pressures permit the assumption of ideal behavior for gases and vapors. In case of unknown final temperatures, such as in the calculation of adiabatic reaction temperatures (theoretical flame temperatures), a trial-and-error solution is usually required.

Combustion calculations are primarily concerned with the determination of air



requirements, excess air, quantity and composition of combustion products, stack (flue) losses, thermal efficiencies, and flame temperatures. In order to determine these quantities with reasonable accuracy for a low-pressure combustion process of a low-sulfur-content fuel in which negligible work is done on or by the system and in which the combustion products consist predominantly of carbon dioxide, oxygen, nitrogen and other inerts, and water vapor (complete combustion), the following data are required: (1) the chemical composition of the fuel; (2) the standard heat of combustion of the fuel; (3) the temperature of the fuel and the air supply when entering the system, and the humidity of the air supply; (4) the carbon dioxide content of the dry flue gas; (5) the flue-gas temperature when leaving the system; (6) the sensible enthalpy changes over the required temperature range of the fuel or its components, water vapor, liquid water, carbon dioxide, oxygen, nitrogen, carbon monoxide, and hydrogen; and (7) the equilibrium constants over the required temperature range and the heats of reaction at a suitable temperature of the reactions:



In case of insufficient air for complete combustion, evaluation of the combustion process can also be made if free carbon and hydrocarbons are not present in the combustion products, if the equilibria in item (7) above can be assumed, and if the temperature at which these equilibria "freeze" is known. This means that the combustion products leaving the system under consideration must consist only of carbon dioxide, carbon monoxide, water vapor, hydrogen, oxygen, and nitrogen and other inerts. The fuel-air ratio is needed in place of item (4) above for this case.

The assumption of negligible sulfur content generally introduces only small errors. Methods for correction of the effects of sulfur will be discussed. The assumptions of carbon- and hydrocarbon-free combustion products usually will not apply to the following types of combustion processes: (1) production of specific furnace atmospheres such as required for metallurgical applications (41), (2) internal-combustion engine processes, and (3) combustion of solid fuels on grates. Excluding these applications, the combustion of fluid or fluidized solid fuels is characterized by the relative completeness of the combustion process due to the intimate mixing and accurate metering of air and fuel which is possible, and simple solutions of the problems normally encountered are, therefore, possible.

Simplifications in the evaluation of combustion processes can be made for hydrocarbon fuels or fuels reducible to the equivalent of a hydrocarbon. The carbon-hydrogen weight ratio, C/H, or its equivalent can be used in such applications as a criterion of fuel composition. By means of the C/H ratio it is possible to express air requirements, excess air, stack losses, flame temperatures, and many other combustion variables in the form of simple equations and graphs. Further, for liquid hydrocarbon fuels, heats of combustion, heats of formation, specific heats, and other thermal properties are also functions of the C/H ratio (18,19,22). This makes the C/H ratio an extremely valuable parameter in combustion calculations, particularly, since it can be estimated with sufficient accuracy from standard A.S.T.M. tests (1,2). See also *Calorimetry; Hydrocarbons; Thermochemistry; Thermodynamics; Units*.

### Definitions, Units, and Nomenclature

In the following sections the pound-mole will be used as basic unit for gaseous fuels and the pound for liquid and solid fuels. The basis of one pound of pure hydrocarbon or hydrocarbon equiva-

lent will also be employed. The ideal gas laws are assumed to hold except for calculations of composition, heat of combustion, and specific gravity or density of fuel gases containing hydrocarbons. Deviations from the ideal gas laws are considerable for most hydrocarbon gases and vapors. In calculations based on partial volumes (Amagat's Law) for gases containing such materials, ideal gas law heating values and specific gravities should be used when gas analyses are given in mole per cent. These ideal values should be corrected by the ideal gas law deviations corresponding to the proper total pressure of the various components and the gas temperature when the analyses are given in volume per cent. For accuracy in combustion methods of gas analysis, the nonideal behavior of carbon dioxide should also be considered (4,32).

In the application of the first law of thermodynamics to combustion calculations for processes other than those taking place in internal-combustion engines, the following definitions and conventions are usually accepted:

(1) A *system* refers to a substance or group of substances inside of real or ideal boundaries.

(2) A *process* refers to the changes taking place in the system.

(3) *Heat of Reaction*. Evolution of heat,  $Q$ , is designated as positive. If  $\Delta H^0$  is the total enthalpy change of a system referred to given standard reference states for a flow process proceeding with negligible kinetic and potential energy changes and with no significant amounts of electrical and mechanical work done on or by the system, or a nonflow process proceeding at constant pressure, then:  $\Delta H^0 = -Q$ .

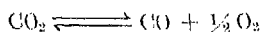
(4) *Standard Reference States*. For gases and vapors, the standard reference state is the ideal gas state at 1 atm. (equivalent to unit fugacity) and 60°F. (520°R.). For water and normally liquid fuels, it is the liquid state at 1 atm. and 60°F. The standard heat of combustion ( $-\Delta H_c^0 = Q_p$ ) is then the heat release at constant pressure for an oxidation process yielding the gases carbon dioxide and sulfur dioxide and liquid water, with all reactants and products at their standard reference states.

The following symbols and nomenclature will be employed in this article:

$a$	= mole fraction of hydrocarbons in dry fuel gas
$b$	= mole fraction of carbon monoxide in dry fuel gas
$c$	= mole fraction of hydrogen in dry fuel gas
C/H	= carbon-hydrogen weight ratio of a hydrocarbon mixture or a hydrocarbon-hydrogen mixture
C/H*	= modified C/H ratio = (wt. % C + 0.375 wt. % S)/(wt. % H - 0.126 wt. % O) = wt. % carbon equivalent/wt. % net hydrogen
$C_nH_m$	= general chemical formula of a hydrocarbon mixture
$d$	= mole fraction of oxygen in dry fuel gas
$e$	= mole fraction of nitrogen in dry fuel gas
$f$	= mole fraction of carbon dioxide in dry fuel gas
$F$	= weight fraction of hydrocarbon equivalent = $0.01(\text{wt. \% C} + 0.375 \text{ wt. \% S} + \text{wt. \% H} - 0.126 \text{ wt. \% O})$
$g$	= moles of dry air per mole of dry fuel gas
$h$	= total moles of water vapor per mole of dry fuel gas
$H^0$	= sensible enthalpy referred to ideal state (zero pressure) at 60°F. (520°R.)
$\Delta H^0$	= enthalpy change due to chemical reaction or change of state with enthalpies of reactants and products referred to standard reference states
$K$	= equilibrium constant for ideal gaseous system
$m$	= number of hydrogen atoms per average molecule of hydrocarbon mixture
$n$	= number of carbon atoms per average molecule of hydrocarbon mixture
$n_1$	= stoichiometric moles of carbon dioxide per mole of dry fuel in combustion products
$n_2$	= stoichiometric moles of water vapor per mole of dry fuel in combustion products + $h$
$n_3$	= stoichiometric moles of nitrogen per mole of dry fuel in combustion products
$n_4$	= stoichiometric moles of oxygen per mole of dry fuel in combustion products
$N$	= total moles of combustion products per mole of dry fuel = $n_1 + n_2 + n_3 + n_4 + n_1x/2 + n_2y/2$
$p$	= partial pressure of gaseous component, atm.
$P$	= mole fraction of carbon dioxide plus sulfur dioxide in dry flue gas
$Q$	= available heat per unit quantity of fuel
$t$	= temperature, °F.

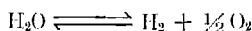
$T$  = absolute temperature,  $^{\circ}\text{R.}$ ,  $= t + 460$

$x$  = fraction of carbon dioxide dissociated according to the equation:



$X$  = fraction excess air = moles excess air/moles theoretical air

$y$  = fraction of water vapor dissociated according to the equation:



$\pi$  = total pressure, atm.

The highest accuracy in the physical constants used in this discussion is not necessary for most engineering applications. Below are summarized the physical constants and fundamental data that will be employed:

(1) Composition of air is assumed to be 20.9 mole per cent oxygen and 79.1 mole per cent atmospheric nitrogen for the purpose of combustion calculations. These values are normally indicated by Orsat analyses.

(2) The conversion factor from one pound-mole of dry ideal gas to cubic feet at 60 $^{\circ}$ F. and 30.00 inches of 32 $^{\circ}$ F. mercury (standard cubic feet, S.C.F.) is 0.0026422 and the factor for moles of dry gas per mole of gas saturated with water vapor at 60 $^{\circ}$ F. and 30.00 inches of 32 $^{\circ}$ F. mercury is 0.9826. The complete conversion factor from pound-moles to standard conditions for gas measurement is therefore 0.0025962.

(3) Atomic weights are from the 1941 International Tables except for the assumption that hydrogen = 1.0 and carbon = 12.0 in some formulas for simplified combustion calculations.

(4) The B.t.u. is defined as 1055 joules (abs.).

### Enthalpies of Fuels, Their Combustion Products, and Air

The sensible enthalpies (heat contents) of fluid fuels over a limited temperature range are required for stack-loss, thermal-efficiency, and flame-temperature calculations when the fuels are at temperatures other than one of the standard reference temperatures for enthalpy and heat of combustion data. When more accurate data are not available, enthalpies above 520 $^{\circ}$ R. of gaseous hydrocarbons with three or more carbon atoms can be estimated by the specific-heat equation proposed by Edmister (7) as shown below:

$$H^0_{520} = (T - 520)(2.56 + 0.51n) + \\ [(2.78 \times 10^{-5})T^2 - 7.50][13n^2 + 44n - 6.5mn + 49.5m - 57] \quad (1)$$

For methane, ethane, and ethylene, Sweigert and Beardsley (26) propose enthalpy equations of the form:

$$H^0_{520} = \alpha(T - 520) + \beta\{T^2 - (2.704 \times 10^6)\} \quad (1a)$$

For methane,  $\alpha = 4.52$ ,  $\beta = 0.003685$ ; for ethane,  $\alpha = 4.01$ ,  $\beta = 0.00818$ ; and for ethylene,  $\alpha = 4.23$  and  $\beta = 0.005885$ . All units are in B.t.u.,  $^{\circ}\text{R.}$ , and pound-moles; and the enthalpies are for the ideal-gas state, that is, at zero pressure.

For liquid hydrocarbons with C/H ratios from 4.5 to 12.0, the heat content above 60 $^{\circ}$ F. can be estimated from the C/H ratio and the temperature,  $t$ , in  $^{\circ}\text{F.}$ , by a revision of an existing correlation (18):

$$H^l_{60} = [0.0006105t^2 + 0.916t - 57.2][0.160/(C/H - 3.85) + 0.387] \quad (2)$$

where  $H$  is the sensible enthalpy above 60 $^{\circ}$ F. in B.t.u./lb. The C/H ratios can be estimated from simple physical tests (17,22). Similar correlations of enthalpies of

liquid- and gaseous-petroleum fractions with physical properties by Watson and Nelson (27) and Hanson and Hurd (9) are widely used.

The enthalpies expressed in B.t.u./lb.-mole of nitrogen, oxygen, carbon monoxide, hydrogen, carbon dioxide, and water vapor referred to the ideal gases at 60°F. (520°R.) are summarized in Table I. The data for carbon monoxide can also be used for air. These values are based on enthalpies referred to 540°R. reported by Heek which were derived from specific-heat data obtained from spectroscopic measurements (10). They are reported to more significant figures than warranted by their accuracy and are only applicable at low pressures. A comparison between the older specific-heat data and those based on spectroscopic analysis can be found in a paper by Sweigert and Beardsley (26).

Modern and complete summaries of specific heat, enthalpy, and many other thermodynamic data for gases and gaseous and liquid hydrocarbons, can be found in references (11,40).

Specific heats of cokes and coals differ widely with composition but fall generally in a 0.25–0.38 B.t.u./(lb.)(°F.) range at 60°F. and increase approximately 0.0002 per °F. in the 60–2000°F. range.

TABLE I. Sensible Enthalpies of Flue-Gas Components.<sup>a</sup>

Temperature, °R.	Heat content for ideal-gas state, B.t.u./lb.-mole <sup>b</sup>					
	N <sub>2</sub>	O <sub>2</sub>	CO (air)	H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O
520	0	0	0	0	0	0
600	557	563	558	554	723	641
700	1,255	1,276	1,259	1,249	1,675	1,451
800	1,955	2,000	1,961	1,945	2,678	2,270
900	2,659	2,736	2,667	2,643	3,726	3,100
1,000	3,370	3,485	3,382	3,343	4,813	3,944
1,100	4,089	4,249	4,108	4,044	5,935	4,803
1,200	4,815	5,025	4,843	4,746	7,089	5,678
1,300	5,550	5,812	5,588	5,450	8,272	6,568
1,400	6,293	6,611	6,342	6,156	9,481	7,474
1,500	7,044	7,419	7,105	6,865	10,714	8,396
2,000	10,934	11,571	11,049	10,467	17,170	13,252
2,500	14,992	15,852	15,159	14,194	23,961	18,513
3,000	19,167	20,231	19,378	18,069	30,979	24,111
3,500	23,426	24,692	23,672	22,075	38,151	29,993
4,000	27,744	29,232	28,019	26,200	45,429	36,100
4,500	32,106	33,841	32,406	30,421	52,790	42,370
5,000	36,503	38,522	36,825	34,727	60,221	48,783

<sup>a</sup> Calculated from data in ref. (10).

<sup>b</sup> Reference temperature = 520°R.

### Heat of Combustion

The standard heats of reaction at constant pressure for combustion of inorganic fuel gases and many gaseous and liquid hydrocarbons have been determined with great accuracy by Rossini and his co-workers of the National Bureau of Standards and, together with selected values from other sources, have now been summarized in reference (40). They are reported on a mole or weight basis at a reference temperature of 25°C. Other summaries of such heat of combustion data may be found in the textbooks given as general references in the bibliography. Conversion of molar heats of combustion to

a volume basis requires information on the pressure-temperature-volume relationships of the gases in question and, for conversion to the 60°F. basis, specific-heat or enthalpy data for the fuels, carbon dioxide, oxygen, and water or water vapor must also be known. Data of this type can be found in reference (38). In general, heating values on a volume basis are given at a pressure of 30 in. Hg, and it must be remembered that deviations from the ideal gas laws are considerable for hydrocarbons containing two or more carbon atoms per molecule. However, mass spectrometer and automatic, low-temperature fractional-distillation methods yield analyses in terms of mole per cent (distillation proceeds under sufficiently reduced pressure to prevent deviations from ideal gas behavior). In combustion analyses, hydrocarbons are determined at partial pressures difficult to evaluate because of dilution with nitrogen or air (4). In Table II, a summary of the most frequently required heating values based on recent data is presented. The estimated values at 30 in. Hg pressure are based on a correlation which assumes deviations from ideal volumes proportional to the molecular weight of the hydrocarbons.

Below are summarized empirical equations for the standard heat of combustion at 60°F. and constant pressure (liquid water and gaseous carbon dioxide as products) of various hydrocarbon gases (derived from data given in reference (40)). These equations are recommended for application to gas analyses which report only the class and carbon number,  $n$ , or average carbon number of the hydrocarbons.  $\Delta H_c^0$  is in units of B.t.u./lb.-mole and can be converted to other units and nonideal conditions as discussed above.

*Paraffins* ( $C_nH_{2n+2}$ ):

$$-\Delta H_c^0 = 282,400n + 106,800 \quad (n = 2-7) \quad (3)$$

$$-\Delta H_c^0 = 288,200n + 95,200 \quad (n = 1-2) \quad (4)$$

*Monoolefins* ( $C_nH_{2n}$ ):

$$-\Delta H_c^0 = 280,100n + 46,800 \quad (n = 2-7) \quad (5)$$

*Acetylenes* ( $C_nH_{2n-2}$ ):

$$-\Delta H_c^0 = 279,400n \quad (n = 2-7) \quad (6)$$

*Alkylbenzenes* ( $C_nH_{2n-6}$ ):

$$-\Delta H_c^0 = 275,900n - 235,300 \quad (n = 6-9) \quad (7)$$

While the heating value of gaseous fuels is generally determined with a constant-pressure, flow-type calorimeter, a bomb-type calorimeter is employed for liquid and solid fuels. Although the resulting heating value is the heat of combustion at constant volume, a correction to constant pressure is usually not made in industrial practice since it is normally less than 40 B.t.u./lb. The correction from constant volume to constant pressure can be made by adding 2.60 B.t.u. per weight per cent net hydrogen content (wt. % hydrogen - 0.126 wt. % oxygen) to the heat of combustion per pound of fuel at constant volume and 60°F. Occasionally, the net heat of combustion is used in thermal-efficiency calculations. This is the heat of reaction when burning the fuel at unit pressure and 60°F. to form the gases carbon dioxide and water vapor at the same conditions. Since the heat of vaporization of water is approximately 1059.8 B.t.u./lb. under these conditions, 94.8 B.t.u./lb. of fuel per weight per cent of total

hydrogen must be subtracted from the standard heat of combustion to give the net heat of combustion as defined above.

Empirical methods for estimating the heat of combustion of liquid petroleum fractions of satisfactory accuracy are available. Cragoe (5) correlated heat of combustion with the specific gravity; Hougen and Watson (12) used the U.O.P. characterization factor which can be obtained from the specific gravity and viscosity or the specific gravity and mean average boiling point (25,27,28). Linden and Othmer (18) correlated the heat of combustion of liquid hydrocarbons at constant pressure, 60°F., water as liquid ( $\Delta H_c^\circ$  in B.t.u./lb.) with the carbon-hydrogen weight ratio, C/H, in the equation:

$$-\Delta H_c^\circ = [1/(C/H + 1)][59,020 + 12,320 C/H + 197.8 (C/H)^2] \quad (8)$$

TABLE II. Heats of Combustion of Fuel Gases.

Gas	Molecular weight	Standard heat of combustion, $-\Delta H_c^\circ$				
		B.t.u./lb.-mole	B.t.u./S.C.F. (ideal gas)		B.t.u./S.C.F. (real gas)	
			Dry	Saturated	Dry	Saturated
Hydrogen	2.016	123,021	325.0	319.4	324.9 <sup>b</sup>	319.5 <sup>b</sup>
Carbon monoxide	28.01	121,636	321.4	315.8	321.6 <sup>b</sup>	316.0 <sup>b</sup>
Methane	16.042	383,160	1,012.4	994.8	1,014.6 <sup>b</sup>	996.9 <sup>b</sup>
Ethane	30.068	671,230	1,773.5	1,742.6	1,789 <sup>b</sup>	1,758 <sup>b</sup>
Propane	44.094	955,240	2,524	2,480	2,573 <sup>b</sup>	2,529 <sup>b</sup>
Butane	58.120	1,238,510	3,272	3,215	3,392 <sup>b</sup>	3,333 <sup>b</sup>
2-Methyl propane	58.120	1,235,550	3,264	3,208	3,363 <sup>b</sup>	3,304 <sup>b</sup>
Pentane	72.146	1,521,400	4,020	3,950	4,200 <sup>c</sup>	4,120 <sup>c</sup>
Ethylene	28.052	607,010	1,603.8	1,575.9	1,614 <sup>b</sup>	1,586 <sup>b</sup>
Propene	42.078	885,560	2,340	2,299	2,383 <sup>b</sup>	2,342 <sup>b</sup>
1-Butene	56.104	1,169,570	3,090	3,036	3,190 <sup>c</sup>	3,130 <sup>c</sup>
2-Butene <sup>d</sup>	56.104	1,165,720	3,080	3,026	3,180 <sup>c</sup>	3,120 <sup>c</sup>
2-Methyl propene	56.104	1,163,000	3,073	3,019	3,170 <sup>c</sup>	3,120 <sup>c</sup>
1-Pentene	70.130	1,452,340	3,837	3,771	4,000 <sup>c</sup>	3,930 <sup>c</sup>
Benzene	78.180	1,419,980	3,752	3,687	3,930 <sup>c</sup>	3,870 <sup>c</sup>
Toluene	92.134	1,698,080	4,487	4,409	4,750 <sup>c</sup>	4,670 <sup>c</sup>
Acetylene	26.036	558,860	1,476.6	1,450.9	1,488 <sup>b</sup>	1,462 <sup>b</sup>
Propyne	40.062	833,390	2,202	2,164	2,250 <sup>c</sup>	2,210 <sup>c</sup>

<sup>a</sup> Calculated from data given in ref. (40).

<sup>b</sup> From ref. (38).

<sup>c</sup> From estimated deviations from ideal gas law, uncertainty of 1% or less.

<sup>d</sup> Average of cis and trans isomers.

This equation is based on a correlation of the heat of formation of liquid hydrocarbons with their C/H ratio. For fuel oils, an empirical correction to allow for nonhydrocarbon constituents which corresponds to a factor of  $(1.047 - 0.0074 C/H)$  is applied to equation (8). In Figure 1 the gross (standard) heating values for pure liquid hydrocarbons and fuel oils are given as a function of their C/H ratio as calculated from equation (8). This correlation was tested against known data (6,20) and was found to have an arithmetic average deviation of approximately 0.5%.

The C/H ratio of liquid hydrocarbon fuels is best determined by one of the ultimate analysis methods employing a combustion train (8), but simple and accurate methods for estimating C/H ratios from standard A.S.T.M. physical tests have been developed. The correlation by Watson, Nelson, and Murphy (28) (U.O.P. K factor)

for estimating the per cent hydrogen from average boiling point and gravity or the recently published method (17,22) which permits direct nomographic estimates of C/H ratios from one of three groups of standard A.S.T.M. tests (2) (aniline point-gravity-50% boiling point, gravity-average boiling point, gravity-viscosity) are useful for this

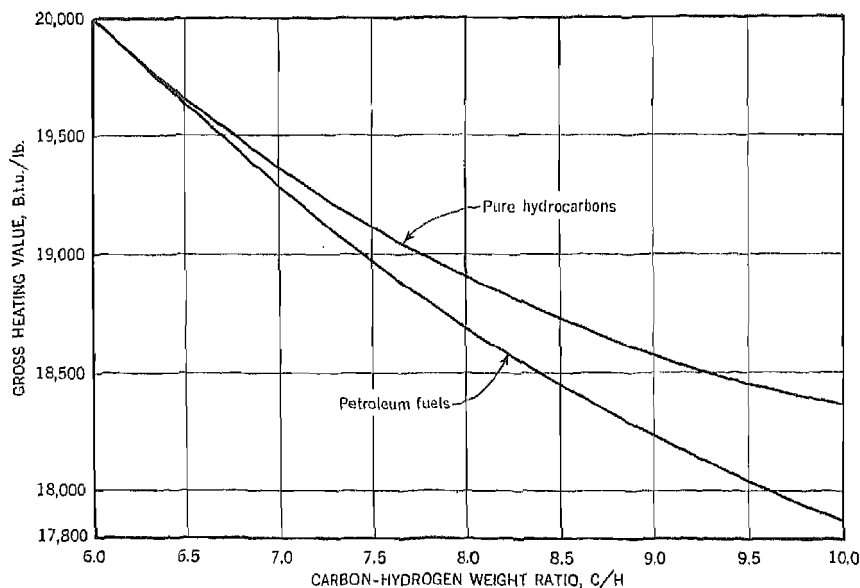


Fig. 1. Heat of combustion of liquid hydrocarbon fuels.

purpose. When the U.O.P. K factor method is used, an assumption of 99% hydrocarbons for distillate oils and 98% hydrocarbons for residual oils should be satisfactory. For combustion calculations it is usually sufficiently accurate to use the values for the C/H ratio given in Table III.

TABLE III. Approximate C/H Ratios for Liquid Fuels.

Type of fuel	C/H ratio
Natural gasoline.....	5.2
Straight-run gasoline.....	5.6
Cracked gasoline.....	6.0
Kerosene.....	6.3
No. 1 fuel oil.....	6.3
Gas-house gas oil.....	6.3
Light Diesel oil.....	6.3
No. 2 fuel oil:	
35° A.P.I.....	6.6
30° A.P.I.....	7.0
No. 3 fuel oil.....	7.3
Bunker C fuel oil:	
12° A.P.I.....	8.0
10° A.P.I.....	8.5
8° A.P.I.....	9.0

A number of empirical equations for estimating heats of combustion of coals as functions of their ultimate or proximate analyses have been developed (23). Since a

complete ultimate analysis is more difficult than the determination of the heat of combustion, the Dulong-type equations for estimating heats of combustion of coals are actually more useful for simplification of ultimate analyses (23). For this purpose a revised form of Dulong's equation can be used:

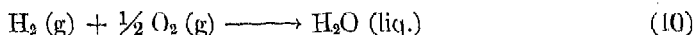
$$-\Delta H_c^0/\text{lb. of carbon equivalent} = 14,500 + 61,000/(\text{C}/\text{H}^*) \quad (9)$$

where  $-\Delta H_c^0$  is the standard heat of combustion. Although C/H\* is based entirely on stoichiometric considerations (3) (equivalence of 12.01 lb. of carbon and 32.06 lb. of sulfur and the assumption that oxygen is bound as water), it appears to correlate well with the heat of combustion. In order to estimate C/H\*, the heat of combustion and the carbon and sulfur contents of the coal would be necessary. However, for combustion calculations, it is usually sufficiently accurate to use the values based on the rank of coal (1,21) given in Table IV. If sulfur is neglected, the carbon and net hydrogen contents can then be calculated from the actual heat of combustion and equation (9).

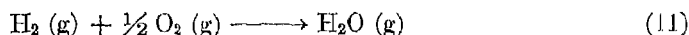
**TABLE IV. Estimated C/H\* Ratios for Coal.**

Rank	C/H*	Rank	C/H*
Anthracite.....	40	Bituminous.....	20
Semianthracite.....	30	Subbituminous.....	20
Semibituminous.....	20	Lignite.....	30

Standard heats of reaction for the combustion reactions given below are also frequently required in thermochemical calculations. These heats of reaction were calculated from those at 25°C. (77°F.) and the required heat-capacity data as given in reference (40). The values are given to more significant figures than warranted by their accuracy.



$$-\Delta H_c^0 \text{ at } 60^\circ\text{F.} = 61,022.1 \text{ B.t.u./lb. or } 123,021 \text{ B.t.u./lb.-mole}$$



$$-\Delta H_c^0 \text{ at } 60^\circ\text{F.} = 51,551.5 \text{ B.t.u./lb. or } 103,928 \text{ B.t.u./lb.-mole}$$



$$-\Delta H_c^0 \text{ at } 60^\circ\text{F.} = 14,086.5 \text{ B.t.u./lb. or } 169,179 \text{ B.t.u./lb.-mole}$$



$$-\Delta H_c^0 \text{ at } 60^\circ\text{F.} = 4,342.6 \text{ B.t.u./lb. or } 121,636 \text{ B.t.u./lb.-mole}$$

The designations (g) and (liq.) refer to the standard gas and liquid states. From equations (10) and (11) the heat of vaporization of water is 1,059.8 B.t.u./lb. or 19,093 B.t.u./lb.-mole at 60°F. and 1 atm. to form water vapor at unit fugacity.

It should be noted that in general the difference between heats of reaction based on the standard gaseous state of unit fugacity and the real gas state at one atmosphere pressure is equivalent to or less than the uncertainty of the experimental measurements. For engineering application to low-pressure processes, enthalpy data based

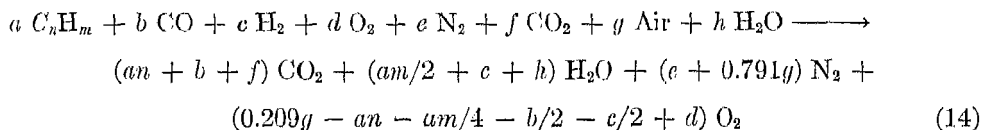


on ideal gas behavior therefore require no correction except for deviation from the ideal gas law in mole or weight to volume conversions.

### Air Requirements, Excess Air, and Flue-Gas Analyses

The control of combustion processes is generally based on flue-gas analyses obtained with a simple Orsat-type gas analyzer capable of analyzing for carbon dioxide, oxygen, and carbon monoxide on a dry basis and nitrogen by difference (see *Gas analysis*) (32). Frequently, where automatic gas-analysis equipment is used, only the carbon dioxide content can be obtained. Since gaseous, liquid, and fluidized solid fuels when employed for the generation of heat energy are generally burned under conditions resulting in complete combustion, relationships between fuel composition, excess air, and carbon dioxide content of the flue gas (dry basis) can be developed. Such relationships are valuable for checking the efficiency of the combustion process. For maximum efficiency the fuel usually has to be burned at the minimum excess air which permits complete, smoke-free combustion.

For complex gaseous fuels which are essentially sulfur-free, the general combustion equation given below holds for the condition of complete combustion:



The following relationships hold for the gaseous fuel given in equation (14) for the case of complete combustion:

$$\text{Moles theoretical air/mole of gas} = 4.78(an + am/4 + b/2 + c/2 - d) \quad (15)$$

$$\text{Moles excess air/mole of gas} = [(1 - P)/P][an + b + f] -$$

$$3.78(an + am/4 + b/2 + c/2 - d) - e \quad (16)$$

$$\text{Moles total air/mole of gas} = (1/P)(an + b + f) +$$

$$am/4 - b/2 + c/2 - f - d - e \quad (17)$$

Maximum fraction carbon dioxide =

$$\frac{an + b + f}{an + b + f + e + 3.78(an + am/4 + b/2 + c/2 - d)} \quad (18)$$

Fraction excess air,  $X$  = equation (16)/equation (15) =

$$\frac{[(1 - P)/P][an + b + f] - e}{4.78(an + am/4 + b/2 + c/2 - d)} - 0.791 \quad (19)$$

$$\text{Fraction excess air, } X = \frac{\% O_2 (an + b + f)}{\% CO_2 (an + am/4 + b/2 + c/2 - d)} \quad (20)$$

The mole fraction of carbon dioxide in the dry flue gas,  $P$ , can be assumed to be equivalent to the volume fraction. Considerable simplification of the above expressions is possible when less complex fuels are used.

For hydrocarbon fuels and coals the relationships between air requirements, excess

air, maximum mole fraction carbon dioxide in the dry flue gas, and the flue-gas analysis can be greatly simplified for the case of complete combustion by the use of the C/H ratio or its equivalent as basic criterion. For some types of residual fuel oils and for coals or coke, the C/H\* ratio must be used to correct for the presence of sulfur, oxygen, and incombustibles. Whenever sufficient nonhydrocarbon constituents are present to justify the use of the C/H\* ratio, the equations for air requirements and other quantities defined on a unit weight basis given below have to be multiplied by the weight fraction of hydrocarbon equivalent,  $F$  (see "Nomenclature"). When combustion is complete except for the appearance of carbon in the refuse, the C/H\* ratio and the fraction of hydrocarbon constituents can be based on a fictitious carbon content, equivalent to the weight per cent carbon actually burned, for applications to be discussed subsequently.

In addition to petroleum oils and coals, the expressions given below are also applicable to natural and liquefied petroleum gases and oil gases containing only a trace of carbon monoxide or carbon dioxide. An Orsat analyzer will give the value of  $P$  directly if a nonaqueous displacement fluid is used. Errors will be introduced by the use of an aqueous gas-displacement fluid when analyzing flue gases from high-sulfur fuels.

$$\text{Moles CO}_2 + \text{SO}_2/\text{lb. of fuel} = (F) \left[ \frac{C/H^*}{12(C/H^* + 1)} \right] \quad (21)$$

$$\text{Moles H}_2\text{O}/\text{lb. of fuel} = \frac{F}{2(C/H^* + 1)} \quad (22)$$

$$\text{Moles of theoretical air}/\text{lb. of fuel} = \frac{F}{0.209} \left[ \frac{C/H^* + 3}{12(C/H^* + 1)} \right] \quad (23)$$

$$\text{Moles of excess air}/\text{lb. of fuel} = (F) \left[ \frac{C/H^* - 4.78P(C/H^*) - 11.35P}{12P(C/H^* + 1)} \right] \quad (24)$$

$$\text{Moles of air}/\text{lb. of fuel} = (F) \left[ \frac{C/H^* + 3P}{12P(C/H^* + 1)} \right] \quad (25)$$

$$\text{Maximum fraction CO}_2 + \text{SO}_2 = \frac{C/H^*}{4.78 C/H^* + 11.35} \quad (26)$$

$$\text{Fraction of excess air, } X = \frac{0.209 C/H^* - PC/H^* - 2.37P}{P(C/H^* + 3)} \quad (27)$$

$$\text{Fraction of excess air, } X = \frac{3.78 (\% \text{ O}_2)}{100 - \% \text{ CO}_2 - 4.78 (\% \text{ O}_2)} \quad (28)$$

$$C/H^* = \frac{P[3(X + 1) - 0.63]}{0.209 - P(X + 1)} \quad (29)$$

If combustion is complete except for the appearance of carbon monoxide and hydrogen in the flue gas, equation (28) can be modified as follows:

$$\text{Fraction of excess air, } X = \frac{3.78 [\% \text{ O}_2 - 0.50 (\% \text{ CO} + \% \text{ H}_2)]}{100 - \% \text{ CO}_2 - 4.78 (\% \text{ O}_2) + 0.89 (\% \text{ CO} + \% \text{ H}_2)} \quad (30)$$

For complete combustion, the total moles of combustion products per pound of fuel can be obtained from the sum of equation (21) + equation (22) + 0.791(equation (23)) + equation (24) which is equal to  $P(6P + C/H^*)/12P(C/H^* + 1)$ .  $P' = 0.98$  to 1.00 for most types of liquid-petroleum oils derived from American crude oils, and the assumption of  $P' = 1.00$  will introduce negligible errors for such fuels. The  $C/H^*$  ratio is then equal to the actual  $C/H$  ratio which can be estimated from simple physical tests (17,22). The effect of nitrogen impurities on the mole fraction of carbon dioxide in the dry flue gas,  $P$ , is usually within the limits of accuracy of Orsat analyses, and equations (24), (25), (26), (27), (28), and (29) will give good approximations up to 30 wt. % of nitrogen content. For example, the maximum fraction of carbon dioxide for methane ( $C/H = 2.98$ ) is 0.116 or 11.6% by equation (26). For a mixture of 80 mole per cent methane and 20 mole per cent nitrogen (69.6 and 30.4 wt. %, respectively), the actual maximum Orsat carbon dioxide would be 11.3%. This error of 0.3% carbon dioxide would be reduced for higher-molecular-weight gases and in the presence of excess air.

$C/H$  ratios of gaseous hydrocarbon fuels can be estimated from a number of flue-gas analyses at varying amounts of excess air, by substituting in equations (28) and (29) and averaging the results. This procedure is not sufficiently accurate for the higher  $C/H$  ratio liquid fuels and reliance on one determination is not recommended.

### Chemical Equilibrium in the Flame and the Flue Gases

At temperatures above 3000°F., and when less than the stoichiometric amount of air or oxygen is supplied, the combustion products can no longer be assumed to consist entirely of carbon dioxide, water vapor, nitrogen, and oxygen. The magnitude of the equilibrium constants for the reactions:



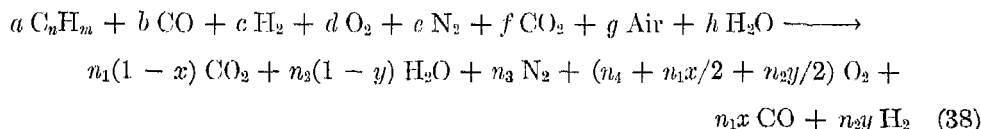
at temperatures normally encountered in combustion processes makes it necessary to consider them in the calculation of flame temperatures, of thermal efficiencies for high-temperature furnaces and some types of internal-combustion engines, and of combustion-product distribution. In general, with the fuel and air at low initial temperatures and sufficient air supply to prevent the presence of hydrocarbons and free carbon in the combustion products, only equations (31) and (32) have to be considered. Wenner (29), however, considers equation (34) as well. At high preheat temperatures and when using higher oxygen concentrations than in air, the secondary dissociation reactions are of importance. In the presence of less than stoichiometric air or oxygen supply, an approximation of the composition of the combustion products at flame (adiabatic reaction) temperature can be made by assuming them to consist only of carbon dioxide, carbon monoxide, water, hydrogen, oxygen, and nitrogen (13). It is then necessary to test the final results of a calculation based on equations (31) and (32) by equation (33) for the presence or absence of carbon formation. If  $p_{\text{CO}_2}$  and  $p_{\text{CO}}$  are the partial pressures of carbon dioxide and carbon monoxide in the final mixtures

and  $K_3$  is the equilibrium constant for equation (33),  $(p_{\text{CO}})^2/p_{\text{CO}_2}$  must be less than  $K_3$  to insure the absence of carbon formation. The value of  $K_3$  at temperature  $T$ , as derived from data by Lewis and von Elbe (16), is approximately:

$$\log K_3 = -15,140/T + 8.81 \quad T = 3,000 \text{ to } 5,400^\circ\text{R.} \quad (37)$$

It is usually difficult to calculate the composition of the combustion products (flue gases) at temperatures below the flame (adiabatic reaction) temperature since the equilibriums involved freeze at temperatures considerably above those of normal flue-gas exit temperatures due to the rapid decrease in the rates of reaction with decreasing temperature. Hottel *et al.* (11) suggest a "freezing" temperature of  $1600^\circ\text{K.}$  ( $2420^\circ\text{F.}$ ,  $2880^\circ\text{R.}$ ). By the use of such a known "freezing" temperature it is possible to calculate the approximate composition of combustion products for all lower temperatures.

For a moist fuel consisting of hydrocarbons, carbon monoxide, hydrogen, oxygen, nitrogen, and carbon dioxide which is burned with humid air, the combustion reaction excluding effects of dissociation was given in equation (14). The revised combustion equation allowing for dissociation is:



where:  $n_1 = am + b + f$ ,  $n_2 = 0.500am + c + h$ ,  $n_3 = e + 0.791g$ , and  $n_4 = 0.209g - am - 0.250am - 0.500b - 0.500c + d$ . If less than the stoichiometric quantity of air is used, the value of  $n_4$  would be negative. The values of  $g$  for the desired excess or deficiency of air can be calculated from equations (15), (16), and (17).

Assuming the ideal gas law to hold and denoting the equilibrium constant for the dissociation of  $\text{CO}_2$  as  $K_1$  and that for the dissociation of  $\text{H}_2\text{O}$  as  $K_2$ , it follows that at a total pressure of  $\pi$  atmospheres the state of equilibrium will be expressed by:

$$K_1 = \frac{x}{1-x} \left[ \left( \frac{\pi}{N} \right) (n_4 + n_1x/2 + n_2y/2) \right]^{1/2} \quad (39)$$

$$K_2 = \frac{y}{1-y} \left[ \left( \frac{\pi}{N} \right) (n_4 + n_1x/2 + n_2y/2) \right]^{1/2} \quad (40)$$

where:

$$x = \frac{K_1y}{K_2 - K_2y + K_1y} \quad (41)$$

It is permissible to neglect the  $x/2$  and  $y/2$  terms in  $N$  for combustion in air because of the relatively large value of  $n_3$ .

The equilibrium constants for equations (31) and (32) can be approximated by the following expressions:

$$\log K_1 = (-25.6 \times 10^3)/T + 4.26 \quad T = 3400 \text{ to } 5400^\circ\text{R.} \quad (42)$$

$$\log K_2 = (-23.8 \times 10^3)/T + 3.09 \quad T = 3400 \text{ to } 5400^\circ\text{R.} \quad (43)$$

These equations were developed by averaging data of Lewis and von Elbe (16), Zeise (30), and Zeise and Khodshaian (31). Based on more recent data of Hottel *et al.*, the constants in equation (42) are  $-26.0 \times 10^3$  and 4.36, respectively, those in equation (43) are  $-23.75 \times 10^3$  and 3.06. For the determination of the composition of the combustion products from a fuel of known composition at a given temperature and fuel-air ratio, it would be necessary to solve equations (38), (39), (40), (41), (42), and (43) simultaneously. (The case of unknown temperature will be discussed under flame temperatures.) This procedure is only an approximation since (1) the existence of equilibrium is assumed and (2) the presence of only a limited number of chemical species is assumed. If the assumption of Hottel *et al.* (11) is adopted, no further change in composition occurs below temperatures of approximately 2900°R. and the values for  $K_1$  and  $K_2$  at that temperature can be substituted in equations (39), (40), and (41) for solutions in this region.

Considerable simplification of the determination of the extent of dissociation is possible for the case of combustion of fuels at theoretical air requirements. For these conditions the equilibriums  $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$  and  $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$  can be assumed not to affect each other and can then also be assumed to occur under the partial pressure  $p$  of undissociated carbon dioxide or water vapor. If  $z$  is the fraction of carbon dioxide or water dissociated and  $K$  is the corresponding equilibrium constant for equation (31) or (32):

$$\frac{z^2}{(1-z)^2(2+z)} = \frac{K^2}{p} \quad (44)$$

From a plot of equation (44) and the equilibrium constants obtained from equations (42) and (43), it is then quite simple to obtain an approximation of the fraction dissociated using calculated partial pressures of carbon dioxide,  $\pi n_1/N$ , and water vapor,  $\pi n_2/N$ , in the flue gases, from equation (38). Linden and Othmer (19) developed empirical equations for the extent of dissociation in the combustion of hydrocarbon fuels with the theoretical amount of air at one atmosphere total pressure. It was assumed that the fuel is a pure hydrocarbon and burned with dry air and that the dissociation of carbon dioxide and water follows equation (44). The same basic enthalpy, heat of combustion, and dissociation data as presented here were used. This derivation was based on the fact that the C/H ratio of the fuel determines the variation of the partial pressures of carbon dioxide and water in the flue gases. The derived equations for the approximate extent of dissociation for fuels ranging from 3 to 12 C/H ratio at temperatures from 3100 to 4500°R. were:

$$x = [(4.63 \times 10^{-33})T^{8.685} - 0.0051] \left[ 0.358 + 0.730 \log \frac{4.78 \text{ C/H} + 17.35}{\text{C/H}} \right] \quad (45)$$

$$y = [(1.558 \times 10^{-33})T^{8.685} - 0.00120] \left[ 0.333 + 0.758 \log \frac{4.78 \text{ C/H} + 17.35}{6} \right] \quad (46)$$

### Thermal Efficiencies of Combustion Processes

In order to define the thermal efficiency of a combustion process, the terms in the following expression and the system it applies to must be defined:

$$-\Delta H_c^0 = H_P - H_R + Q \quad (47)$$

$-\Delta H_c^0$  is the standard heat of combustion per unit quantity of fuel.  $H_R$  is the sum of the sensible and latent enthalpies of the combustion reactants and inerts when entering the system, and  $H_P$  is the sum of the sensible enthalpies plus the standard heats of combustion and vaporization of the combustion products and inerts when leaving the system, all referred to the same quantities and reference states as  $-\Delta H_c^0$ . The system is defined as the burner, the combustion chamber, and the flue passages up to the point where the heat-exchange area stops.  $Q$  is, therefore, the heat quantity leaving the system through the heat-exchange area and such areas of the combustion chamber and flue passages not employed as useful heat-exchange area.

The thermal efficiency,  $E$ , of a combustion process employed to generate heat only, with no significant quantity of work done on or by the system, can then be defined as heat output over heat input or:

$$E = \frac{Q}{-\Delta H_c^0 + H_R^*} = \frac{-\Delta H_c^0 + H_R^* - H_P}{-\Delta H_c^0 + H_R^*} \quad (48)$$

The asterisk indicates that according to accepted conventions the latent heat of vaporization of water introduced into the system in vapor form should be subtracted from  $H_R$ . On the basis of the definition of equation (47),  $Q$ , the available heat per unit quantity of fuel does not depend on the utilization of the heat release of a combustion process and is, therefore, a criterion of the combustion efficiency of the burner and of the heat exchange between the flue gases and the ducts through which they pass. Direct measurement of  $Q$  is generally not feasible. For instance, in a boiler installation it would be necessary to measure the conduction, convection, and radiation losses as well as the enthalpy change for the conversion of feed water to steam. In intermittent operation the gap between useful heat and  $Q$  widens even further due to warm-up losses. It should be noted that for the same operating conditions,  $E$  in equation (48) will be a function of the reference conditions and reference states (35,36). In American practice, the reference conditions are usually 60°F. and 30 in. Hg pressure, and the reference states are the ideal gases for carbon dioxide, carbon monoxide, hydrogen, oxygen, and nitrogen and liquid water. Vaporization of water is assumed to occur at 60°F. at a  $\Delta H_v$  of 1,059.8 B.t.u./lb. or 19,093 B.t.u./lb.-mole.

In the combustion of fluid fuels the total stack loss is equivalent to the total enthalpy of the combustion products,  $H_P$ . For the general combustion reaction of a gaseous fuel including the effects of dissociation and incomplete combustion (see eq. (14) and (38)) one obtains therefore:

$$H_P = n_1(1-x) H_{CO_2}^0 + n_2(1-y) (H_{H_2O}^0 + 19,093) + n_3 H_{N_2}^0 + (n_4 + n_1x/2 + n_2y/2) H_{O_2}^0 + n_1x (H_{CO}^0 + 121,636) + n_2y (H_{H_2}^0 + 123,021) \quad (49)$$

and similarly:

$$H_R = a H_{C_nH_m}^0 + b H_{CO}^0 + c H_{H_2}^0 + d H_{O_2}^0 + e H_{N_2}^0 + f H_{CO_2}^0 + g H_{Air}^0 + h (H_{H_2O}^0 + 19,093) \quad (50)$$

The various enthalpies are in units of B.t.u./lb.-mole referred to 60°F. The enthalpies contributing to the stack loss,  $H_P$ , are computed at the flue-gas temperature. Identical relationships on a unit-volume or unit-weight basis can be derived easily and the ideal gas laws can be assumed if this assumption is made consistently, that is, ideal gas heating values and analyses corrected to zero pressure must be used. The thermal

efficiency (excluding work terms) and stack loss of a combustion process can then be obtained for the most general case by using equation (48) in conjunction with equations (38), (39), (40), (41), (42), (43), (49), and (50) and the necessary heat of combustion and enthalpy data. Up to 3000°F., dissociation effects may be neglected at stoichiometric air or oxygen supply, while above 3000°F. the direct method of equation (44) can be used to approximate the fractions of carbon dioxide and water dissociated,  $x$  and  $y$ , respectively. With increasing quantities of excess air, the limit for neglecting dissociation is further extended due to suppression of dissociation reactions. It is therefore possible to set  $x$  and  $y$  in equations (38) and (49) equal to zero in most cases, which results in considerable simplification.

For hydrocarbon fuels, fuels consisting of hydrogen and hydrocarbons, or for coals and coke, further simplification of thermal-efficiency, stack-loss, and adiabatic reaction-temperature calculations is possible by the use of the C/H or C/H\* ratio as a parameter.

Linden and Othmer (19) developed a stack-loss correlation for complete combustion and reference conditions of 60°F., water as a liquid, and dry air by dividing the calculation of total stack loss per pound of fuel,  $H_P$ , into minimum stack loss,  $L_{min.}$ , and stack loss due to excess air,  $L_x$ :

$$H_P = L_{min.} + L_x \quad (51)$$

Then, by substituting empirical heat-content equations for nitrogen, carbon dioxide, water vapor, and air as functions of absolute temperature,  $T$ , taking into account the latent heat of vaporization of the water vapor formed and employing the suitable relationships given in the section on air requirements, excess air, and flue-gas analyses, the following expressions were obtained:

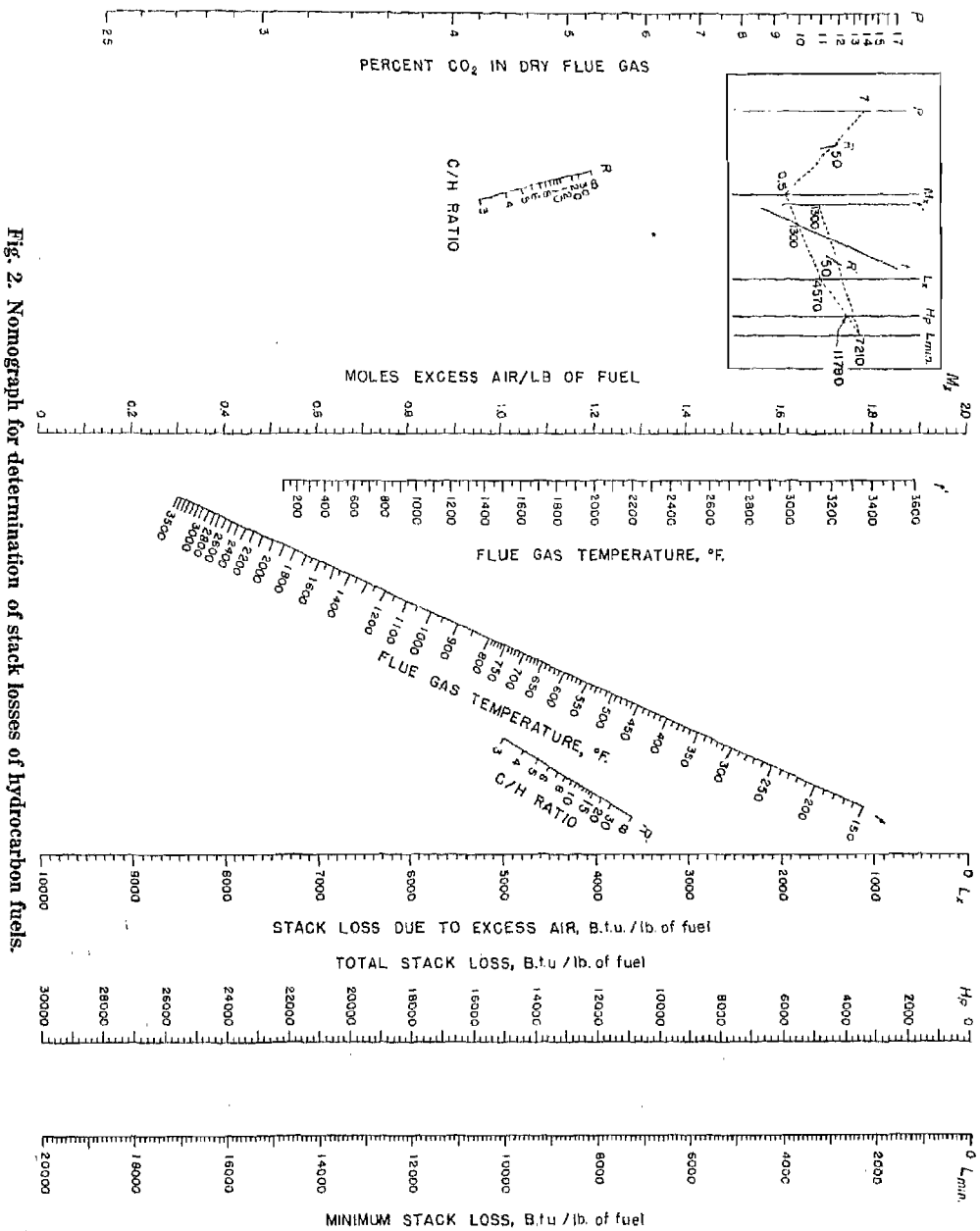
$$L_{min.} = T^{1.24}(1.655 + 0.474 \text{ C/H})/(\text{C/H} + 1) + (5900 - 1043 \text{ C/H})/(\text{C/H} + 1) \quad (52)$$

$$L_x = (2.060T^{1.16} - 2850)[(\text{C/H} - 4.78P/\text{C/H} - 11.35P)/12P(\text{C/H} + 1)] \quad (53)$$

The estimated maximum error of equations (52) and (53) for a flue temperature range from 250 to 3500°F. was given as 2%. For a large part of the normal operating range (500–2000°F. stack temperature) the error was expected to be much lower, usually in the range of 1%. Equations (52) and (53) were presented in nomographic form (19) and a revised copy of this nomograph is shown in Figure 2.

The use of this nomograph is illustrated in the following example: Given:  $\text{CO}_2 = 7.0\%$ , C/H ratio = 5.0, flue-gas temperature = 1300°F. To obtain the minimum stack loss, draw a line from the  $t'$  scale through the  $R'$  scale to the  $L_{min.}$  scale. The intersection, 7,210 B.t.u./lb. of fuel, is the minimum stack loss. For stack loss due to excess air, a line drawn from the  $P$  scale through the  $R$  scale to the  $M_x$  scale and then from this scale through the  $t$  scale and intersecting the  $L_x$  scale gives the result, 4,570 B.t.u./lb. of fuel. Total stack loss is obtained by adding  $L_x$  and  $L_{min.}$  on the  $H_P$  scale, giving 11,780 B.t.u./lb. of fuel. For flame temperatures, assume flue-gas temperatures until  $H_P$  equals the gross heat of combustion of the fuel.

For gases consisting primarily of hydrocarbons and nitrogen (high-inert natural gases) or of hydrocarbons, hydrogen, and nitrogen (refinery oil gases and some high-B.t.u. oil gases), Figure 2 can be used if the constituents other than hydrocarbons and hydrogen do not exceed 30 weight per cent. The C/H ratio of the hydrocarbon-





hydrogen fraction must then be calculated and the resulting stack loss multiplied by the weight fraction of hydrocarbon-hydrogen constituents in the fuel gas,  $F$ , to convert to a one pound of total fuel basis. If the percentage of the heat of combustion lost in the stack gas is desired ( $100H_P/(-\Delta H_c^0)$ ), the stack loss obtained directly from the nomograph (that is, on a 100% hydrocarbon-hydrogen basis or  $F = 1$ ) must be divided by the heat of combustion per pound of inert-free gas. The same procedure applies to water-vapor content of the gas. Only traces of carbon dioxide or carbon monoxide are permissible because of their effect on the per cent carbon dioxide in the flue gas. Water-vapor content of the combustion air should be taken into consideration by multiplying the sensible enthalpy of the water vapor at stack temperature (see Table I) by the moles of water vapor in the air supply per pound of fuel (see eq. (25)) and adding the result to the stack loss.

For example, if a high-inert natural gas consisting of 70 mole per cent methane, 15 mole per cent ethane, and 15 mole per cent nitrogen is burned completely with dry air to give an Orsat analysis of 8% carbon dioxide, and the stack temperature is 1040°F., what is the stack loss referred to standard reference conditions?

*Solution:*

$$\text{Molecular weight of gas} = (0.70)(16.04) + (0.15)(30.07) + (0.15)(28.02) = 19.94$$

$$\text{Wt. \% of hydrocarbons} = 78.9 \text{ or } F = 0.789$$

$$\text{Wt. \% of nitrogen} = 21.1$$

$$\text{C/H ratio of hydrocarbons} = \frac{12.01[(0.70)(1) + (0.15)(2)]}{1.008[(0.70)(4) + (0.15)(6)]} = 3.22$$

$$\text{Heat of combustion of total gas} = (0.70)(383,160) + (0.15)(671,230) = 368,900 \text{ B.t.u./lb.-mole}$$

$$\text{Heat of combustion of nitrogen-free gas} = 368,900/(0.789)(19.94) = 23,400 \text{ B.t.u./lb.}$$

$$\text{Minimum stack loss from Figure 2, } I_{min.} = 7,170 \text{ B.t.u./lb. of N}_2\text{-free gas}$$

$$\text{Stack loss due to excess air from Figure 2, } L_x = 1,870 \text{ B.t.u./lb. of N}_2\text{-free gas}$$

$$\text{Total stack loss, } H_P = 9,040 \text{ B.t.u./lb. of N}_2\text{-free gas}$$

$$\text{Per cent stack loss (assuming no nitrogen in fuel gas)} = 9,040/23,400 = 38.6$$

If the nitrogen in the gas is taken into consideration, the moles of nitrogen per pound of nitrogen-free gas ( $21.1/78.9 \times 28.0 = 0.00955$ ) have to be multiplied by the enthalpy of nitrogen at 1040°F. ( $0.00955 \times 7,044 = 67 \text{ B.t.u./lb.}$ ), and this value added to the total stack loss per pound of nitrogen-free gas. It can be seen that if this correction is neglected an error of only +0.7% (38.9 versus 38.6% stack loss), or less than the accuracy of the basic data, would result. If the air supply contained 0.0174 mole of water vapor per mole of dry air, a larger error would result if it were neglected. From equation (25) the air supply is 0.855 mole per pound of inert-free gas. The sensible enthalpy of the water vapor is 8,396 B.t.u./lb.-mole (see Table I). The stack loss due to moisture in the air is then 125 B.t.u./lb. of inert-free gas or nearly double that due to 15% of nitrogen in the fuel gas.

A similar approach can be taken for fuels containing large quantities of sulfur, oxygen, ash, and moisture. The C/H\* ratio must then be used and the stack loss based on the C/H\* ratio corrected to a one pound of actual-fuel basis by multiplication with the factor  $F = 0.01(\text{wt. \% carbon equivalent} + \text{wt. \% net hydrogen})$ . The total oxygen content can be assumed to be bound as water in liquid form, and its heat of vaporization,  $\Delta H_v$ , should be taken into account whenever the analytical data are available to establish the combined free and bound moisture content. This is done by multiplying  $\Delta H_v = 1,059.8 \text{ B.t.u./lb.}$  by a factor of 1.126 times the weight fraction of total oxygen. The sensible enthalpy at stack temperature of the water vapor and other inerts derived from the fuel can normally be neglected.

When comparing thermal efficiencies of combustion equipment, it is important to

take variations of the enthalpies of the fuel and combustion air,  $H_R$ , into account. Changes in the absolute humidity of the air are significant as has been shown above.

The methods for the calculation of stack losses based on the C/H or C/H\* ratio of petroleum fuels, oil gases, or coals are not applicable if combustion is not complete, that is, if the combustion products leaving the system contain significant quantities of materials other than carbon dioxide, water or water vapor, sulfur dioxide, nitrogen, oxygen, and combustible-free ash. High flue-gas exit temperatures or insufficient oxygen supply will cause the production of significant quantities of carbon monoxide, hydrogen, and possibly free carbon as determined by the chemical equilibriums involved and the extent to which they are approached. In combustion of solid fuels on grates, combustion is normally incomplete due to insufficient contact of fuel and oxidant, which results in combustible material being present in the solid combustion products (refuse or cinders). For these cases, standard enthalpy and material balances as discussed in detail in the textbooks by Hougen and Watson (36) and Haslam and Russell (35) must be used.

If combustion of coal is complete except for the appearance of carbon in the refuse, the methods for calculating stack losses which have been presented are still applicable. In such a case the  $F$  factor and the C/H\* ratio should be based on the weight per cent carbon actually burned.

### Flame Temperatures

According to Wenner's treatment of this subject (29), theoretical flame temperatures are of importance in engineering considerations because they represent the maximum possible temperatures or potentials at which the thermal energy produced by a given combustion process will be available for conversion to work, and because the magnitude of the temperature is an important consideration in the choice of materials of construction for furnaces.

The temperatures which can be calculated with existing methods are actually adiabatic reaction temperatures of simultaneous reactions. They would represent the optimum obtainable temperatures if conduction, convection, and radiation losses were the only additional factors. However, it is generally not practical to consider all the possible dissociation reactions, and the assumption that equilibrium in respect to all the reactions is reached simultaneously may not be valid.

In spite of these factors, adiabatic reaction temperatures calculated by the standard methods closely approach actual flame temperatures. The calculation can be based on the same system of equations and thermochemical data used in the section on thermal efficiencies by setting  $Q$  in equation (47) equal to zero. A trial-and-error solution is required. It is most convenient to assume a series of temperatures and solve for the fraction of carbon dioxide and water vapor dissociated using equations (39), (40), and (41). The required equilibrium constants can be obtained from equations (42) and (43) and the quantities of reaction products per mole of fuel for a given fuel-air ratio are calculated by means of equation (38). Equation (47) as amplified by equations (49) and (50) can then be rearranged, noting that for adiabatic conditions  $Q = 0$ :

$$-\Delta H_c^0 + H_R - H_P = Q \quad (54)$$

Substituting the proper enthalpy data and the calculated values of  $x$  and  $y$  into  $H_F$  corresponding to the temperatures chosen, equation (54) can be plotted as  $Q = f(T)$ . The temperature corresponding to  $Q = 0$  is then the adiabatic reaction temperature. For combustion with negligible amounts of excess air, a simpler procedure can be used if the dissociation equilibria are assumed to be unaffected by whatever residual or dissociation oxygen is present. The partial pressures of undissociated carbon dioxide,  $\pi n_1/N$ , and water vapor,  $\pi n_2/N$ , can be calculated from equation (14) and used with a plot of equation (44). Results of an application of these methods to a complex fuel can be found in reference (24).

For the case of combustion of hydrocarbon fuels at atmospheric pressure with stoichiometric air requirements, considerable simplification of the calculation of flame temperatures is possible if it is assumed that the equilibria  $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2} \text{O}_2$  and  $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2} \text{O}_2$  do not affect each other.

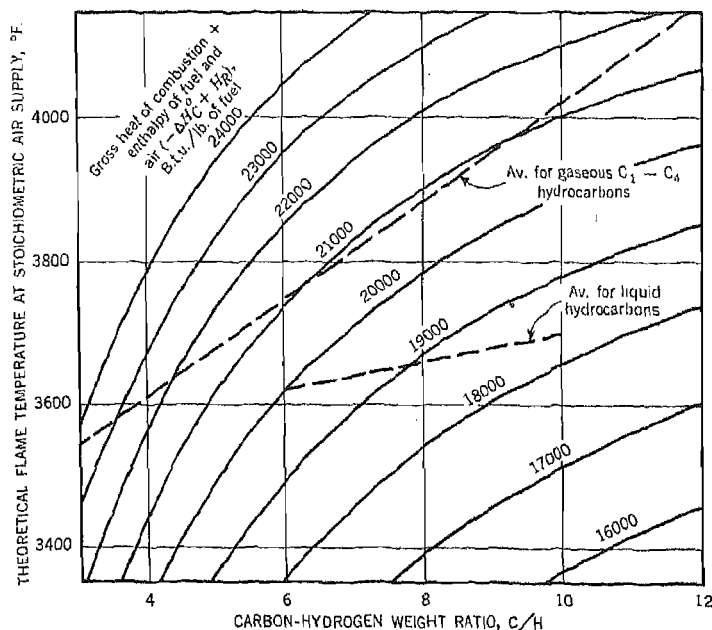


Fig. 3. Theoretical flame temperatures of hydrocarbons at stoichiometric air supply, reference temperature 60°F.

By using empirical expressions for dissociation losses of hydrocarbon fuels at theoretical air supply based on equations (45) and (46), average heats of dissociation for the normal flame-temperature range, and an expression equivalent to equation (52) except for minor modifications for the high-temperature range, two equations of the form:

$$T^{0.685} f_1 (C/H) + T^{1.24} = v \quad \text{and} \quad Q_R f_2 (C/H) - f_3 (C/H) = v$$

were obtained by Linden and Othmer (19) ( $v$  represents an auxiliary variable and  $Q_P$  the gross heat of combustion at constant pressure and 60°F.). A nomograph based on these equations was also presented. It eliminates the need for trial-and-error solutions in the calculation of flame temperatures at stoichiometric proportions of air and

hydrocarbon fuels. By the same method a diagram was prepared (see Fig. 3) which permits estimates of flame temperatures for hydrocarbon or hydrocarbon-hydrogen fuels from their C/H ratio and heat of combustion.

When using Figure 3 or the published nomograph (19) for fuels containing sulfur, nitrogen, oxygen, moisture, and possibly mineral matter, it is necessary to use the C/H\* ratio and to correct the heat of combustion ( $Q_P = -\Delta H_c^h$ ) to a 100% hydrocarbon or hydrocarbon equivalent basis by dividing it by the factor  $F$  (see Fig. 1 for liquid petroleum fuels). A close approximation of the flame temperature at stoichiometric air requirements, which is also an approximation of the maximum flame temperature for a 60°F. burner-inlet temperature, is obtained by this method. The magnitude of the error caused by neglecting the enthalpy of nonhydrocarbon constituents at flame temperature is usually small. For example, for methane saturated with water vapor at 60°F. and 30 in. Hg, the decrease of flame temperature is approximately 5°F. For gases of higher molecular weight, the decrease of flame temperature due to saturation of the gas with water vapor at the same conditions is considerably less. Similarly, nitrogen contents commonly found in natural gases will have effects of less than 50°F. However, large quantities of moisture or its equivalent in oxygen content will affect dissociation and introduce additional uncertainties. Fuel and air temperatures above 60°F. can be corrected for when using Figure 3 by adding the enthalpy of one pound of fuel (referred to 60°F.) and of the dry air supply per pound of fuel to the heat of combustion of the fuel ( $-\Delta H_c^h + H_R$ ). Effects of air humidity can only be estimated by subtracting from the heat of combustion the difference of the enthalpies of the water vapor in the air supply per pound of fuel at the flame temperature and the burner-inlet temperature. The effect of water vapor from air humidity on dissociation losses must again be neglected.

Table V gives a comparison between the flame temperature at theoretical air requirements determined from Figure 3 and calculated flame temperatures (13,14,29). Experimental flame temperatures (maximum and at stoichiometric fuel-air ratios)

TABLE V. Comparison of Calculated and Actual Flame Temperatures.

Fuel	$-\Delta H_c^h$ B.t.u./lb. <sup>a</sup>	C/H ratio	Flame temperatures at theoretical air requirements, °F.			Observed maximum flame temperature, °F. <sup>e</sup>
			Empirical <sup>b</sup>	Observed <sup>c</sup>	Calculated <sup>c</sup>	
Methane	23,885	2.98	3,550	3,390	3,470	3,407
Ethane	22,324	3.97	3,600	3,420	3,490	3,443
Propane	21,664	4.47	3,615	3,480	$\begin{cases} 3,540 \\ 3,621^d \end{cases}$	3,497
Butane	21,309	4.77	3,625	3,400	3,540	3,443
Ethylene	21,639	5.96	3,800	3,540	3,720	3,587
Propylene	21,046	5.96	3,740	3,515	3,680	3,515
Butylene	20,800 <sup>e</sup>	5.96	3,710	3,500	3,650	3,506
84.5% Acetylene- 15.5% methane	21,711	9.51	4,050	4,030	4,060	4,120
Acetylene	21,465	11.93	4,115	4,120	4,150	4,217

<sup>a</sup> From Table II.

<sup>b</sup> From Figure 3.

<sup>c</sup> Source: references (13,14).

<sup>d</sup> Source: reference (29).

<sup>e</sup> Average of isomers.

obtained by Jones *et al.* using the spectral-line-reversal method first developed by Kurlbaum (15) are also given. Maximum flame temperatures are generally obtained for mixtures slightly on the rich side, a fact which is also supported by the relationships of calculated flame temperatures and the per cent theoretical air (13). Table V indicates that the temperatures calculated by the simplified method and by Lewis *et al.* compare well in spite of considerable changes in the basic thermochemical data and inherent errors in the various assumptions and correlations. The flame temperature of propane calculated by Wenner agrees even better. The differences between the experimental and calculated data are also relatively small considering the many assumptions required for the calculations.

In the presence of excess air, flame temperatures of hydrocarbon or hydrocarbon-hydrogen fuels can be obtained from the gross heating value, the C/H ratio of the fuel, and the nomograph of Figure 2 by a trial-and-error solution if either one of the following two conditions exists: (1) flame temperature not above 3,000°F. and any amount of excess air; (2) flame temperature not above 3,500°F. and 20% excess air or more.

A solution is obtained by assuming various flame temperatures until the minimum stack loss and the stack loss due to excess air add up to the gross heat of combustion of the fuel. The same corrections of the heat of combustion for air and fuel temperatures above 60°F. and humidity hold as discussed previously. For acetylene,  $Q_p = 21,465$  B.t.u./lb., the flame temperature at 50% excess air (11.5%  $\text{CO}_2$  by Orsat) would be approximately 3,430°F. from Figure 2.

For application to problems involving percentages of excess air and final temperatures other than those stated above a linear interpolation can be made between the flame temperature at 30–40% excess air using the nomograph of Figure 2 and the flame temperature at 0% excess air (stoichiometric fuel-air ratio) using Figure 3. The results are of sufficient accuracy for most applications and can be obtained very quickly.

For fuels containing significant quantities of carbon monoxide plus carbon dioxide (carburetted water gas, coke-oven gas, Pacific Coast oil gas, producer gas, and high-blow-run, high-B.t.u. oil gas), the methods outlined for the case of combustion of a complex gaseous fuel must be followed.

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HENRY R. LINDEN

## INTERNAL COMBUSTION FUELS

## Fuel Sources

The development of fuels for internal combustion engines and the development of the engines themselves have been mutually dependent and provide an excellent example of the advantages attained by cooperation between two major industries for the benefit of the consuming public.

Three major types of power cycles, in which the working fluid is provided by burning fuel with air in combustion chambers, have attained widespread adoption. These are the spark-ignited, two- or four-stroke, constant-volume combustion cycle (Otto reciprocating engine cycle); the two- or four-stroke, compression-ignited, limited-pressure combustion cycle (Diesel reciprocating engine cycle); and the steady-flow, constant-pressure combustion process utilizing a gas turbine.

Figure 1 illustrates the simplest essentials for the Otto cycle engine. The four strokes illustrated (intake, compression, power, and exhaust) occur every 720 degrees of crankshaft travel. The sequence in the cycle is: (1) The *intake* stroke, from top dead center (TDC) to bottom dead center (BDC), draws in the metered fuel-air mixture from the carburetor. (2) The *compression* stroke raises the pressure and temperature of the mixture using a compression ratio of about seven. (3) Shortly before TDC, the *ignition* spark is applied, and rapid, but controlled combustion of the fuel-air mixture occurs at the end of the compression stroke and at the beginning of the power stroke (approximating constant-volume combustion). (4) The *power* stroke converts the increased temperature and pressure from the energy liberated by combustion into the mechanical work of the rotating crankshaft. (5) The *exhaust* stroke sweeps the

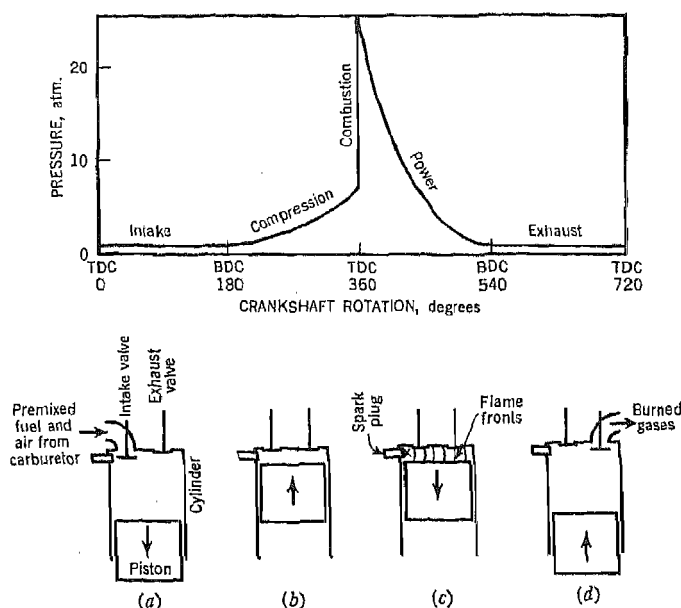


Fig. 1. Pressure-time diagram for Otto cycle engine; engine position shown: (a) end of intake stroke; (b) end of compression stroke; (c) ignition, beginning of power stroke; and (d) beginning of exhaust stroke.

cylinder free of the burned gases. Figure 1 illustrates the process on a pressure-time basis, utilizing degrees of crankshaft travel as an indication of time within the cycle. The temperatures during the cycle are related to the pressure by stoichiometric and thermodynamic relationships.

The early development of Otto cycle engines was stimulated and aided by the availability of manufactured gas as fuel. In 1886, Daimler developed the use of liquid fuel in the Otto cycle engine, which led the way to great expansion in its use in automotive equipment and corresponding changes in refinery technology needed to supply the enormous demands for volatile liquid fuels typified by automotive and aviation gasolines. Volatile fuels are essential for Otto cycle engines to assure a homogeneous fuel-air mixture in the cylinder at the time the spark starts the combustion process, and the chemical composition should be such that the homogeneous mixture burns rapidly, but at a controlled rate. Carburetors have usually been used to provide the

homogeneous fuel-air mixtures, but direct injection of volatile liquid hydrocarbon fuels into the compressed air in the cylinder has been used successfully in spark-ignited Otto cycle engines. This direct injection of fuel does not alter the desired controlled combustion characteristics of the fuel (that is, octane number, and not cetane number, is the criterion for satisfactory combustion characteristics, see p. 945).

Because of the great importance of decreasing both the engine weight per horsepower and the specific fuel consumption to permit maximum range and payload for aircraft, the trend toward restrictive fuel specifications to permit the design of compact, efficient mobile power units has been most pronounced in the case of super-

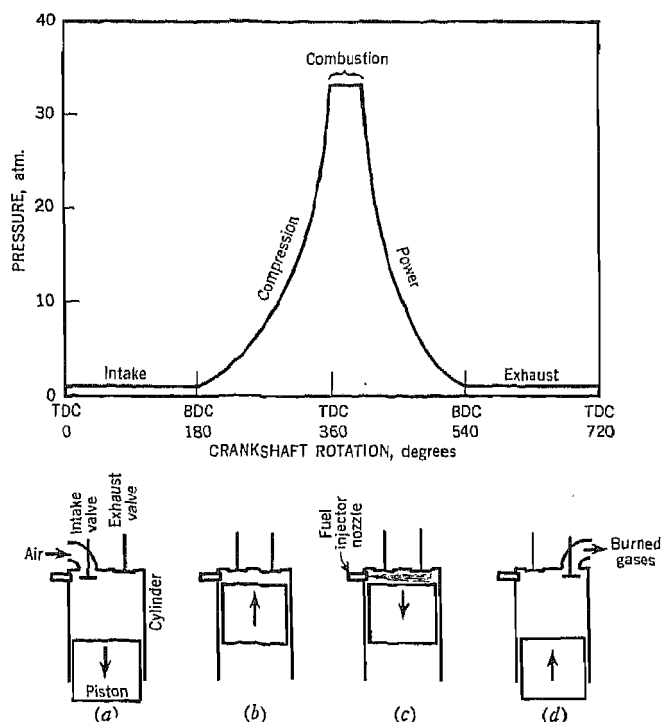


Fig. 2. Pressure-time diagram for Diesel cycle engine; engine position shown: (a) end of intake stroke; (b) end of compression stroke; (c) injection of fuel, beginning of power stroke; and (d) beginning of exhaust stroke.

charged, reciprocating, internal combustion engines for aircraft use. The development of the highest grade of aviation gasoline, grade 115/145, has been possible only by the development of many new synthetic processes of petroleum processing, such as alkylation, catalytic cracking, polymerization, hydrogenation, and isomerization, which resulted in making the petroleum industry the largest producer of synthetic organic chemicals in the world.

Figure 2 gives a simplified schematic illustration of the Diesel cycle. The four strokes illustrated occur every 720 degrees of crankshaft travel, although in two-stroke cycles, the intake and exhaust cycles overlap and occur during the bottom portions of the compression and power strokes, and thus the cycle is complete in 360 degrees of crankshaft travel. The sequence in the four-stroke cycle is: (1) the intake



stroke draws in air alone. (2) The compression stroke, with a compression ratio of about twelve, raises the pressure and temperature of the air to a point where liquid fuel atomized into the cylinder will ignite spontaneously. (3) Injection of the fuel is started during the latter part of the compression stroke, and combustion occurs at a controlled rate such that the pressure remains approximately constant. (4) The power stroke converts the increased temperature and pressure from the energy liberated by combustion into the mechanical work of the rotating crankshaft. (5) The exhaust stroke sweeps the cylinder free of the burned gases. Figure 2 also illustrates the process on a pressure-time basis utilizing degrees of crankshaft travel as an indication of time within the cycle. The temperatures during the cycle are related to the pressure by stoichiometric and thermodynamic relationships.

The early development of the Diesel cycle engines was stimulated and aided by the availability of Scottish shale oils and similar heavy oils from petroleum. The original objective in developing the Diesel engines was to be able to use any low-cost fuel, such as distillate fuel oils, residual fuel oils, and even powdered coal; and large, slow-speed engines have been successfully operated on low-grade fuels. Fuels containing inorganic ash have the serious disadvantage of giving short engine life due to excessive wear and deposits. As the specific output of Diesel engines has been increased, there has been a tendency to require more restrictive specifications for fuels resulting in a decrease in availability and an increase in cost.

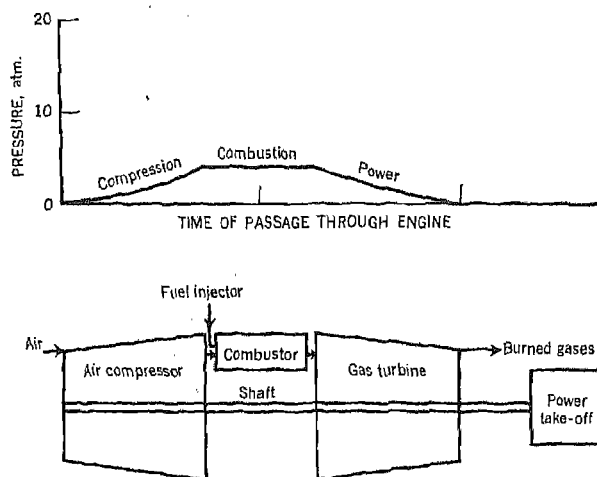


Fig. 3. Pressure-time diagram for gas turbine engine.

Figure 3 illustrates the simplest essentials for the gas turbine engine cycle. This is a steady-flow process involving the following steps: (1) Air is compressed, usually in a centrifugal- or axial-flow compressor with a pressure ratio of about four. (2) Primary combustion air from the compressor is introduced into the combustor where it is mixed with atomized liquid fuel. Original ignition is by means of an electric spark, but the heat of combustion sustains spontaneous ignition when the engine is operating. Secondary air is introduced into the combustor to control the maximum temperature of the burned gases to a safe level for entering the gas turbine. (3) The burned gases expand through the gas turbine which converts the increased temperature, from the

energy liberated by combustion, into mechanical work of the rotating shaft. In contrast to the Otto and Diesel cycles, the increased temperature is used without appreciable increase in pressure over the compression cycle. Part of this mechanical work is utilized to drive the compressor, and the remainder is utilized as the output of the engine. (4) Increased thermal efficiency for the gas turbine engine may be attained by using a heat exchanger to transfer some of the thermal energy from the gases leaving the turbine to the air leaving the compressor before this air enters the combustor. (5) For special application to high-speed aircraft, the gas turbine engine is modified so that the power developed by the combustor gases expanding through the gas turbine is just sufficient to drive the compressor and engine auxiliaries, and the thermal and kinetic energies of the gases leaving the gas turbine are used for jet propulsion to drive the aircraft. Alternatively, some of the power output may be taken from the turbine, and some obtained from the jet, giving the "turbo-prop" system. See "Jet propulsion fuels," p. 954.

Figure 3 illustrates the steady-flow process on a pressure-time basis utilizing the length of the gas turbine engine components as an indication of time. Again the temperatures during the process are related to the pressure by stoichiometric and thermodynamic relationships.

In 1920, the first practical gas turbine engine utilizing liquid petroleum fuel was constructed after about twenty-five years of effort. Improvements in compressor and turbine efficiencies were important in recent rapid advances in this type of engine. Gas turbine engines permit considerable flexibility in design and in type of fuel utilized for stationary, locomotive, or marine-power uses, where weight and space limitations are not too critical. As an extreme case, gas turbines have operated successfully in the Houdry petroleum catalytic cracking process utilizing the catalyst mass containing about 5% of carbonaceous coke as fuel. Coal or coke could be used in a gas producer to make producer gas for use with air in a gas turbine in a stationary power plant. Pulverized coal has potential use in gas turbines for power plants for stationary, locomotive, or marine use; although the presence of ash in the combustion gases may cause serious difficulties in turbine life and efficiency, unless an effective means of removal is developed. Minor inorganic ash in residual petroleum fuel oils may also cause difficulties in turbine life and efficiency. Distillate fuel oils ranging in volatility from Diesel fuels to gasoline appear to be the most satisfactory fuels at present for mobile power plants. By use of heat exchangers to recover heat from the gases leaving the gas turbine, the thermal efficiency may be markedly increased as shown in Figure 4.

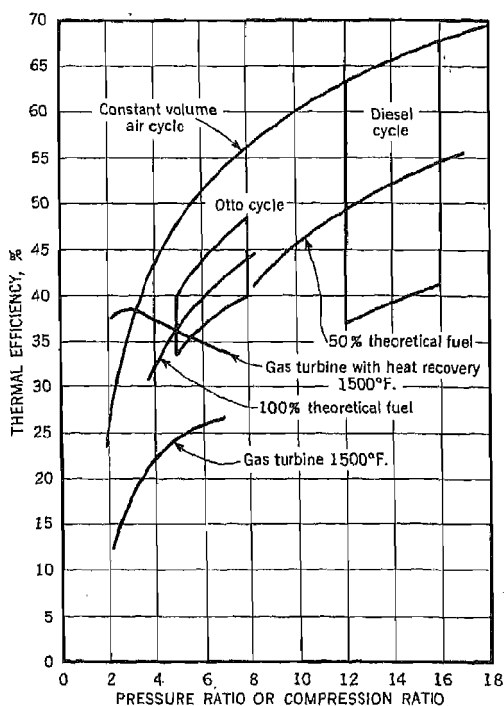


Fig. 4. Thermal efficiency versus compression ratio for Otto cycle, Diesel cycle, and gas turbine engines.

About 98% of the fuel energy used in internal combustion engines is obtained from liquid petroleum fractions, indicating the great advantages of liquid fuels in storage, handling, metering, and combustion. About 50% of our current petroleum production is utilized as fuels for internal combustion engines. Supplies of petroleum are far from inexhaustible, but refinery technology has been developed to a satisfactory industrial level for the production of liquid petroleum products (primarily gasoline) from coal by hydrogenation or Fischer-Tropsch synthesis, from oil shale, from tar sands, and from natural gas. See *Fuels, synthetic liquid; Shale oil*. These sources are estimated to be capable of providing at least one hundred times the potential reserves of the most optimistic estimates of natural petroleum reserves. The synthetic processes for making liquid hydrocarbons from coal or shale would increase the cost of liquid hydrocarbon fuels, but if such processes were adopted to meet demands at some future date, it is probable that liquid fuels tailored to provide improved performance characteristics in Otto, Diesel, or gas turbine cycle engines could be made if engine developments required them. Thus, the long-range picture is not discouraging. If the cost of fuel should increase markedly, it would be expected that refinements in engine design to give higher thermal efficiency or lower specific fuel consumption would increase the demand for improved performance characteristics of fuels. The actual balance is, of course, set by what the consuming public is willing to pay and will vary from one country to another at any one time.

Benzene from the destructive distillation of coal, ethyl alcohol from the fermentation of sugar or starch, partially oxygenated compounds of carbon and hydrogen from petroleum, and similar materials have some potentialities for use as fuels in internal combustion engines. Diisopropyl ether has an octane number of about 100 but, in common with other oxygen-containing liquids, has the disadvantage of lower heating value and thus higher specific fuel consumption, and increased fuel handling problems due to the increased solubility of water in it.

### Fuel Utilization

Internal combustion engines are means of transferring potential energy associated with the fuel-air mixture into kinetic energy available to carry out specific types of work. For reciprocating piston engines, the rate at which the energy is transformed (the power) is a function of the permissible mean effective pressure acting on the pistons, of the piston area, and of the engine speed. The efficiency with which the energy can be transformed (the specific fuel consumption) depends largely upon the temperature levels involved in the thermodynamic cycle of the engine. For reciprocating engines with gas mixtures that closely follow the ideal gas laws, the efficiency depends primarily upon the compression ratio of the engine (that is, the ratio of the total cylinder volume of the combustion chamber with the piston at bottom dead center to the volume of the combustion chamber with the piston at top dead center). For gas turbine engines, the efficiency depends upon the pressure ratio across the compressor and also across the turbine, and upon the maximum permissible temperature for the combustion gases as they enter the turbine. The efficiency of gas turbine engines can be increased by use of heat exchangers to transfer thermal energy between the gases leaving the turbine and the air leaving the compressor and entering the combustion chamber. Figure 4 illustrates typical efficiencies attained by the various power cycles (14).

In most cases of automotive transportation, the propulsion efficiency (efficiency of

transmitting crankshaft energy to driving wheels) is independent of the type of engine or the power cycle used. In the case of high-speed aircraft, the propulsion efficiency of an aircraft propellor drops off rather rapidly at very high speeds (450 m.p.h. or greater). The propulsion efficiency of a high-velocity jet of combustion products, as used in jet propulsion aircraft, improves as the velocity of the aircraft increases. This effect of speed of aircraft upon propulsion efficiency is the major factor in the rapid acceptance of gas turbine jet propulsion engines for high-speed aircraft, despite the lower thermodynamic efficiency indicated in Figure 4. Another major factor is the lower engine weight per horsepower possible with the relatively simple design of the aircraft gas turbine engine.

### General Fuel Performance Criteria

**Heat value** is of prime importance in the performance of a fuel in an internal combustion engine. The heat of combustion of hydrocarbons and of practically all other possible fuels may be easily calculated from readily available thermochemical data on heats of formation. Hydrocarbons have few competitors as far as heating value per pound or gallon of fuel is concerned, particularly when availability is considered. For uses such as automotive transport and jet-propelled aircraft, the fuel is considered on a volume basis which puts a premium on fuels of high C/H ratio, provided all other performance characteristics of the fuel are satisfactory. Aircraft using reciprocating engines are weight-limited rather than volume-limited, which puts a premium on fuels of low C/H ratio (again provided the other performance characteristics are satisfactory).

**Volatility** is of very great importance in the performance of a fuel. In general, fuel volatility, engine design, engine installation and accessories, and the temperature and pressure of the atmosphere at point of use must all be considered and a satisfactory compromise worked out. Barber indicates in Figure 5 typical volatilities of industrially important fuels (2).

Since volatility has a marked effect upon consumer satisfaction in the automobile field, this problem has been studied extensively. A.S.T.M. D86-46 is the generally accepted test method for specifying the volatility characteristics of automotive fuels. This method is a simple batch differential distillation with negligible reflux carried out in a 100-ml. Engler distillation flask with a simple water-cooled condenser. The initial boiling point of the fuel appears to have little significance as far as fuel performance in the engine is concerned. The 10% evaporated point is important in starting in cold weather, in vapor lock of the fuel system, and also in loss of fuel due to vaporization in the carburetor bowl, which leads to decreased mileage. The 50% evaporated point appears significant in time required to warm up the engine to smooth operation, and in the rate of acceleration in normal driving. The 90% evaporated point appears significant in crankcase dilution, and in minimum fuel consumption for reciprocating aircraft engines. The effects of the end point of the fuel appear to be covered by the 90% evaporated point for fuels produced with conventional industrial distillation equipment, although there are some indications that the addition of a few per cent of relatively high-boiling material may have only a minor effect upon the 90% evaporated point, but may cause trouble in reciprocating engines for aircraft.

A.S.T.M. D323-49 gives a procedure for determining the Reid vapor pressure of gasoline. This test measures the vapor pressure of the fuel at 100°F. under carefully

specified conditions. It is roughly proportional to the true vapor pressure of the sample, and it gives indications concerning the loss of gasoline on storage and cold starting.

Since the A.S.T.M. D86 distillation involves distilling the fuel sample in contact with its own vapor and in the absence of air, an *equilibrium air distillation* (E.A.D.) method was developed in the early 1920's to simulate more closely the type of evaporation that occurs in the carburetor and intake manifold of a gasoline engine. Figures 5 and 6 show A.S.T.M. D86 and E.A.D. curves for typical commercial fuels. Barber (2) gives conversion diagrams which permit estimating the E.A.D. curve, provided the A.S.T.M. D86 distillation curve is known. Sample calculations are given which involve material and energy balances comparable to those involved in the psychrometric

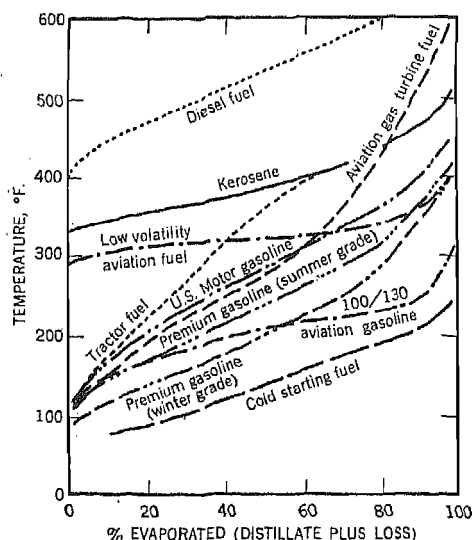


Fig. 5. A.S.T.M. data for a number of internal combustion engine fuels (2).

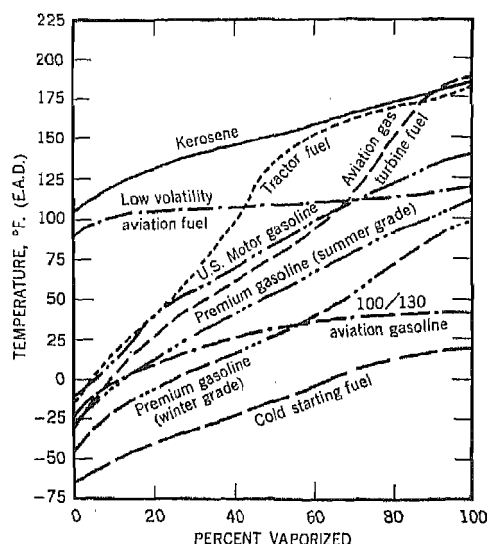


Fig. 6. Equilibrium air distillation values for fuels of varying A.S.T.M. distillations (2).

problem encountered in air conditioning. For specification purposes, the A.S.T.M. D86 is preferable since it is simple and reproducible. The E.A.D. calculations may be valuable for research and trouble-shooting work. Lamb (8) indicates that the A.S.T.M. D86 distillation may be closely approximated by theoretical calculations based on a multicomponent *Rayleigh batch differential distillation*, and the equilibrium air distillation may be closely approximated by theoretical calculations based on a multicomponent *equilibrium flash distillation* at an absolute pressure corresponding to the partial pressure of the fuel in the desired fuel-air mixture. Most petroleum fuels are very complex mixtures of many types of hydrocarbons, but nevertheless, true boiling point distillation data might be converted to A.S.T.M. D86 or to E.A.D. data by extension of this theoretical approach. While the equilibrium air distillation does involve equilibrium distillation into air, the actual evaporation phenomena in the carburetor and intake manifold of internal combustion engines will depend upon both equilibrium and rate phenomena. Further analysis is needed for a complete understanding of the matter (see p. 949, for volatility effects of ethyl fluid).

Most Diesel and gas turbine type internal combustion engines spray liquid fuel droplets directly into the combustion chamber. The motion of the liquid droplets,

their rate of evaporation, the mixing of the fuel vapor with air to give small regions within the flammability limits, and the precombustion and combustion processes all occur in a nonhomogeneous system that is very complex and has so far not been resolved experimentally. The A.S.T.M. D86 distillation provides a reasonable basis for the analysis of engine-fuel performance data; the 10%, 50%, and 90% evaporated points are used for correlations, as with gasoline. Some fuels have been shown to be too volatile and some not volatile enough to give optimum performance in Diesel and gas turbine engines. Engine design and operating variables play a major part in setting the optimum fuel volatility specifications.

**Fluidity** of petroleum fuels is a major factor in their general use. Little trouble occurs with distillate petroleum fuels, generally used in internal combustion engines, except in the most frigid weather. For the more viscous fuels, such as heavy Diesel fuels, fluidity is tested by A.S.T.M. methods for viscosity, cloud and pour point, ash, water, and sediment. A special freezing-point test with a maximum value of  $-67^{\circ}\text{F}$ . is used for aviation gasolines since temperatures near this level are encountered at high altitudes, and, of course, failures in fuel flow cannot be tolerated in aircraft. Fuels having an appreciable ability to dissolve water may cause trouble at low temperatures due to formation of small ice crystals which may clog fuel filters.

**Storage Stability.** As with most organic materials, storage of gasoline for long periods, even at moderate temperatures, may lead to mild oxidation and the formation of gummy materials which may cause trouble in the fuel system of an engine. A.S.T.M. D381-49 gives the procedure for the determination of existent gum, and A.S.T.M. D525-49 and D873-49 give the procedures for evaluating oxidation stability to permit estimating the potential tendency of gasoline to form gum on prolonged storage. Federal Specification Board method 330.1 gives a procedure for a copper-dish gum-stability test which indicates existent gum and the tendency for copper to catalyze gum formation.

**Safety.** Since volatile hydrocarbons are always potential fire hazards, and some additives, such as tetraethyl lead, are poisonous, safety in the handling and use of gasoline must be assured by adequate safe handling procedures. Gasoline stored in tanks with access to air will partially vaporize to form a hydrocarbon-air mixture. A fire or explosion may occur if the resulting fuel-air mixture lies within the explosion limits for the specific fuel. Safety from fire can be assured by maintaining the concentration of the fuel-air mixture on the lean side of the lean explosive limit or on the rich side of the rich explosive limit. For aircraft fuel tanks, which encounter large changes in temperature and in atmospheric pressure as the altitude of the plane changes, this problem can be quite complex and requires more thorough analysis than when all operations are at or near sea level. For example, so-called safety fuel for aircraft with 1.0 lb. Reid vapor pressure may be more hazardous at altitude than conventional aviation gasoline with 7.0 lb. R.V.P. Flash point and fire point test methods measure the tendency of the liquid to vaporize sufficiently to form fuel-air mixtures within the explosive limit range. A flash point of  $100^{\circ}\text{F}$ . is generally accepted as the lowest limit for the safe handling of petroleum fractions without taking special precautions.

The current volume of A.S.T.M. Standards (1) gives standard specifications for motor gasoline, aviation gasoline, Diesel fuels, and other petroleum products, and details of the standardized test methods concerned. Major consumers or producers may also have their own specifications.

## Otto Cycle Engines

**Fuel Performance Limitations.** *Power* (the rate at which energy is transformed) and *economy* (specific fuel consumption or the efficiency with which energy is transformed) are two of the most important characteristics of internal combustion engines and their fuels. As engine design changes are made to increase the power by increasing the mean effective pressure acting on the piston (by increasing compression ratio or by supplying the intake air under increased pressure by supercharging) or to decrease the specific fuel consumption by improving the cycle thermal efficiency (by increasing the compression ratio), uncontrolled combustion phenomena of two types may be encountered: (1) The last part of the fuel which is burned in any one cycle may burn with explosive violence, causing rapid pressure and temperature fluctuations in the gases within the combustion chamber and resulting in a knocking or pinging sound from the cylinder. In a mild case, the sound irritates the driver, causes some loss in power; and, in severe cases, the resulting increase in temperature may cause the engine to fail. (2) Autoignition of the unburned charge in the cylinder may occur due to a hot spot, so that combustion starts before the time set by the spark timing, while the piston is still on its up-stroke, resulting in markedly increased temperatures, which may lead to engine failure in a very short time. Due to the higher working temperatures permitted in cylinder parts of aircraft engines, both knock and preignition are important limiting factors in fuel and engine performance. In automobile engines, the sound effect of knock tends to be the major consideration since the driver usually objects to the sound and alters the engine load to stop the sound before permanent damage from excessive temperatures occurs.

**Knock—Combustion Phenomena.** Fundamentally the controlled and uncontrolled combustion of fuel in an Otto cycle internal combustion engine is a problem in material and energy balances and kinetics of chemical reactions, similar to problems often considered in chemical engineering design for the process industries. Although the reasons are not thoroughly understood, burning up to the time of knock takes place at a comparatively slow (controlled) rate and then, instead of the last part of the charge (the end-zone gases) burning at the same rate, it reacts with explosive rapidity (16). It has been suggested that the change from the controlled combustion is due to compression ignition of the end-zone gases caused by the occurrence of a chain reaction within the end-zone gases with resulting autocatalytic characteristics. From a chemical point of view, the reactions in the end zone should be controlled by the four fundamental factors, temperature, pressure, composition, and time. If these factors could be evaluated for the end-zone gases from the time of their introduction into the intake manifold, through the intake and compression strokes, and through the combustion period up to the time of occurrence of knock, it should be possible to study the effects of fuel composition, engine design, and operating variables in a manner analogous to that used by the chemical engineer who uses laboratory and pilot-plant data to develop satisfactory industrial designs even though the chemical reaction mechanism is not clearly understood. The problem is complicated by the facts that: (1) the reaction mechanisms and energy of activation for the combustion of hydrocarbons are not clear; (2) the operation is cyclic with the entire cycle occurring in about 0.05 second; (3) the pressure and temperature vary greatly through the cycle; and (4) there is a large number of engine design or operating variables, as shown below, that directly or indirectly affect one or more of the four fundamental factors: compression ratio, spark

advance, manifold pressure, cylinder-head temperature, supercharger impeller tip speed, intake-air temperature, engine r.p.m., fuel-air ratio, cooling-fluid temperature and flow rate, intake pressure-exhaust pressure ratio, intake-exhaust valve overlap, latent heat of evaporation of fuel, oil leakage into combustion chamber, nonuniform distribution of high antiknock fuel components in different portions of fuel in the intake system, partial evaporation of fuel in the intake system, nonuniform fuel-air ratio in charge to different cylinders, different temperature sensitivity to detonation of fuel components, design factors affecting the rate of heat flow through cylinder walls, catalytic effects of combustion chamber surfaces, and combustion chamber design to control rate of burning.

**Engine Tests for Knock.** Although the hypothesis that the knock reactions in a gasoline engine are controlled by the temperature, pressure, composition, and time history of the end-zone gases has been found a valuable generalization to aid in estimating the effects of fuel sensitivity and engine severity, the above list of factors that may need to be considered shows clearly why so much emphasis has been placed and work done on the use of highly standardized single-cylinder, knock test engines and the use of the reference fuels, *n*-heptane and isooctane (2,2,4-trimethylpentane), to evaluate and control the antiknock characteristics of gasolines. Normal heptane, a highly knocking fuel, is considered as zero, and isooctane as 100; if a fuel, tested under standard conditions, gives the same result as, for example, a mixture of 30% *n*-heptane and 70% isooctane, its octane value is said to be 70. The development of the standard knock test engines has been carried out since the 1920's through the cooperative Fuel Research Committee sponsored by the Society of Automotive Engineers and the American Petroleum Institute, and during and since War II has been conducted by the Coordinating Research Council, which was established to plan and supervise cooperative research work by the two industries. When a knock test procedure has been developed by C.R.C., the final standardization and publication as a standard for specification use are done by the American Society for Testing Materials. The following four knock test methods have been published by the A.S.T.M. (1): Test for Knock Characteristics of Aviation Fuels by the Aviation Method (D614-49T); Test for Knock Characteristics of Aviation Fuels by the Supercharge Method (D909-48T); Test for Knock Characteristics of Motor Fuels by the Motor Method (D357-48); Test for Knock Characteristics of Motor Fuels by the Research Method (D908-48T). The C.R.C. handbook (5) lists, in addition, several auxiliary test methods and test procedures for full-scale engines on a dynamometer and on the road for research use.

**Engine Severity and Fuel Sensitivity.** The necessity for more than one method of engine antiknock rating is indicated by consideration of the fundamental factors involved in engine severity and in fuel sensitivity. "Engine severity" may be interpreted as the effect of engine design and operating variables upon the temperature, density, and time factors imposed upon the end-zone gases up to the time they are burned normally or to the time knock occurs. Possible catalytic effects due to the surface of the combustion chambers should be included in engine severity. "Fuel sensitivity" may be interpreted as the effect of these overall temperature-density-time factors upon the overall chemical reaction kinetics occurring in the end-zone gases. While the antiknock performance of isooctane varies considerably with a wide variation in engine severity, it is one of the least sensitive fuels and therefore is a desirable reference fuel to use in evaluating antiknock performance of other fuels. Olefinic



hydrocarbons, some aromatic hydrocarbons, and aromatic amines are quite sensitive fuels. In Figure 7, Ryder (12) shows a typical variation of knock-limited output, given as the mean effective pressure (M.E.P.), with charge-air temperature and mixture ratio obtained in a supercharged aircraft engine cylinder. The knock-limited surface shown is for a moderately sensitive fuel such as aviation gasoline, grade 100/130. Isooctane would give a somewhat similar surface, but the vertical variation would be appreciably less. Isooctene (2,4,4-trimethyl-1-pentene) would give a somewhat similar surface, but the vertical variation would be appreciably greater. The figure indicates the variation due to only two of the numerous engine design and operating variables listed above, but somewhat similar effects would be expected for the other variables. It is apparent that the octane number scale is a rubber yardstick whose length in terms of fuel performance in engines varies markedly with engine severity. The problem of making the yardstick the right length is the explanation for the adoption of the four standard methods plus the additional research test methods for the determination of octane number referred to above.

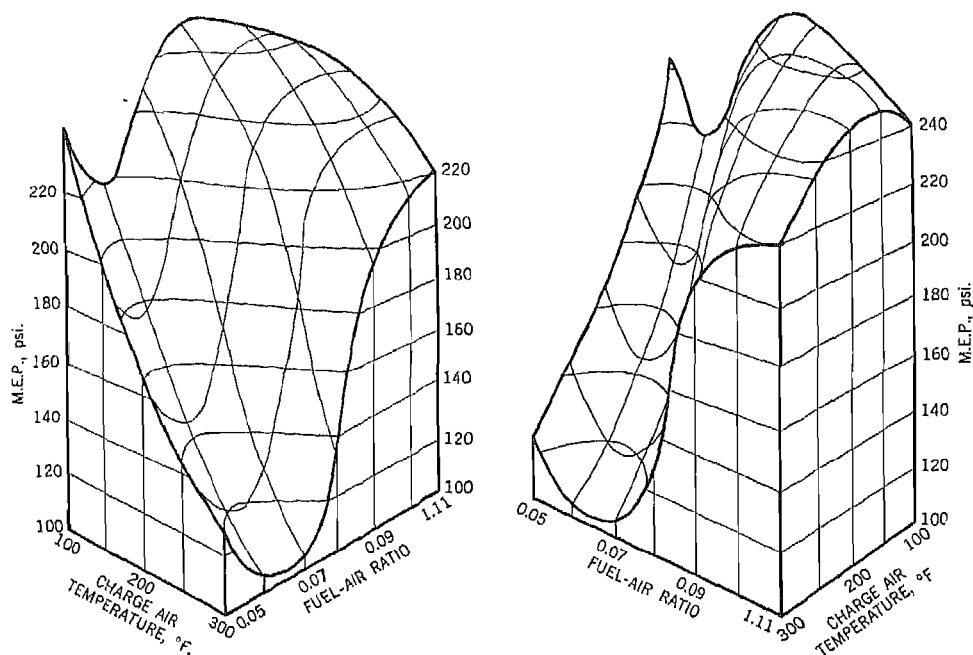


Fig. 7. Variation of detonation-limited output with charge air temperature and fuel-air mixture ratio (12).

The *aviation method* (D614) is conducted at high engine severity conditions by varying the compression ratio at maximum-knock fuel-air ratio and measuring the knocking tendencies by means of the temperature of a thermal plug in the combustion chamber. This method gives fair correlation with the antiknock performance of aircraft fuels in air-cooled engines under cruise or maximum economy operations. This engine severity corresponds roughly to the minimum point in the antiknock surface shown in Figure 7. The *supercharge method* (D909) is conducted at mild engine severity conditions by varying the intake manifold pressure using about 50% excess fuel.

Knock is determined by ear. This method gives fair correlation with antiknock performance of aircraft fuels under take-off or maximum power conditions in aircraft engines, which also utilize 50% excess fuel. Aviation fuel designations such as 100/130 or 115/145 give both the cruise rating (D614) and the take-off rating (D909), in sequence. The *motor method* (D357) is conducted at moderately high engine severity by varying the compression ratio at maximum-knock fuel-air ratio, and determining knock by the bouncing-pin and knock-meter procedure. This motor method was developed to obtain the engine severity that gave best correlations with the road octane numbers determined cooperatively on a group of automobiles in 1932-37. The *research method* (D908) is conducted at mild engine severity by varying the compression

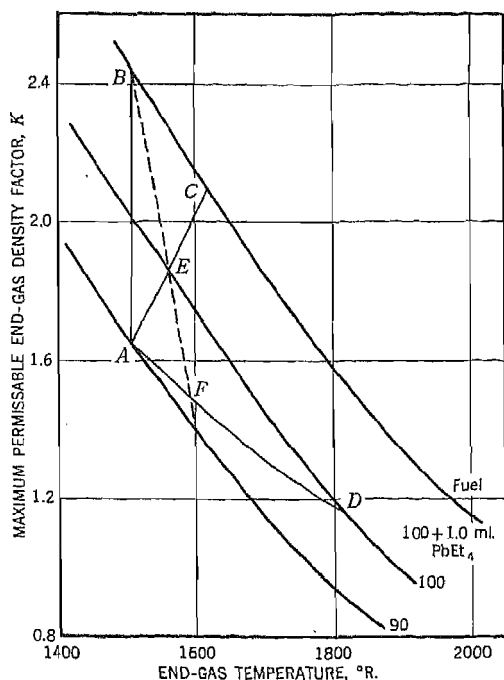


Fig. 8. Maximum permissible end-gas density factor versus end-gas temperature.

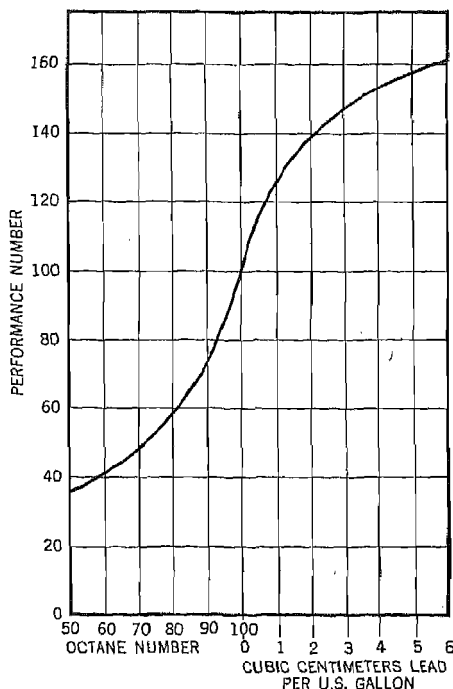


Fig. 9. Performance number versus octane numbers and versus isooctane plus tetraethyl lead.

ratio at maximum-knock fuel-air ratio and determining knock by the bouncing-pin and knock-meter procedure. This method was developed earlier than the motor method and appeared to overrate sensitive fuels compared to early road-test octane numbers. Changes in design of current automobiles have tended to decrease overall engine severity; therefore recent road-test octane numbers appear to be in between those determined in the laboratory by the motor method and by the research method.

These four knock test methods are all conducted in basically the same liquid-cooled cylinder, the engine severity being set at various levels by the operating conditions listed in Table I. Rothrock (11) in Figure 8 shows typical knock-limited fuel-rating curves expressed as functions of the maximum permissible end-gas density factor and end-gas temperature. End-gas density factor includes a proportionality con-

stant  $K$ , characteristic of specific engine parameters used in the test, and may be assumed to be a constant times the true end density. The curves marked 90, 100, and 100 plus 1.0 ml. tetraethyl lead are for the standard octane scale reference fuels. Curve  $AB$  shows the effect of varying only inlet pressure (or supercharging). Curve  $AC$  shows the effect of varying only compression ratio. Curve  $AD$  shows the effect of varying inlet temperature with constant inlet pressure. Curve  $BEP$  shows a typical knock-limited fuel rating curve for a sensitive fuel. The rating of this fuel in terms of the octane scale reference fuels would vary from 100 plus 1.0 ml. tetraethyl lead if tested under engine conditions corresponding to  $AB$ , to 100 octane number if tested under engine conditions corresponding to  $AC$ , to 92 octane number if tested under engine conditions corresponding to  $AD$ .

TABLE I. Operating Conditions for Antiknock Tests.

Operating conditions	Aviation	Supercharge	Motor	Research
R.p.m.	1200	1800	900	600
Spark setting, °BTDC <sup>a</sup>	35	45	26-19	13
Coolant temp., °F.	374	375	212	212
Intake-air temp., °F.	125	125	100	125
Mixture temp., °F.	220	225	300	125
Fuel-air ratio	Max. thermal plug	0.06-0.12	Max. knock	Max. knock
Compression ratio	Variable	7.1	Variable	Variable

<sup>a</sup> Degrees before top dead center.

**Knock Performance Numbers.** As petroleum technology advanced, it became necessary to extend the octane number scale above 100, or pure isooctane. This has been done generally by using isooctane plus up to 6 ml. of tetraethyl lead, although other methods of obtaining a broader scale by inclusion of toluene or triptane (2,2,3-trimethylbutane) have been tried experimentally. One advantage of the heptane-isooctane-tetraethyl lead scale is the relative ready availability of reference fuels for road tests, etc. To avoid confusion, the antiknock rating performance number scale (P.N.) shown in Figure 9, based on an empirical correlation with the reference fuel scale to give some indication of the relative knock-limited engine performance possible in supercharged aircraft engines, was adopted by the military agencies for aviation gasolines, and later extended to include lower octane numbers. This scale shows that the effect upon engine performance of one octane number improvement at the 95 octane number level is markedly greater than the improvement for one octane number at the 75 octane number level.

**Effect of Chemical Composition on Knock.** Between 1920 and the present, many investigators have studied the effect of chemical composition of fuel upon antiknock performance. An excellent 50-page summary of the early work and of the very extensive recent, and previously unpublished, work of American Petroleum Institute Research Project 45 and of the National Advisory Committee of Aeronautics is given by Lovell (10) and should be referred to for details in this important field. In recognition of the effect of engine severity and fuel sensitivity, about 325 individual hydrocarbons, including paraffins (both straight-chain and branched), cycloparaffins, olefins, diolefins, aromatics, bicyclic compounds, etc., have been tested under four or five standardized engine operating conditions. Differences in tendency to knock depend not only upon

the above general chemical families, but there are also large differences between closely related compounds in the same family. Long unbranched carbon atom chains are prone to knock. Branching of the carbon chain or the introduction of an olefinic bond decreases the tendency to knock roughly inversely proportional to the length of the longest unbroken carbon atom chain remaining. Rings are superior to unbranched chains. Superior fuels usually are associated with structural formulas which are compact when drawn in the conventional manner. Such generalizations can be made almost quantitatively. Fundamentally what is involved is the relationship between different types of molecular arrangements and the mechanisms and speeds of their reactions with oxygen under different engine severity conditions. However, the lack of fundamental data on reaction mechanisms, energies of activation, and temperature, pressure, and time factors involved in the actual engines has necessitated the empirical basis of attack that has predominated in this field for the last twenty-five years.

Brown (4), Hottel and Eberhardt (7), and Taylor (14) discuss the use of thermodynamic and chemical equilibrium data for the analysis of phenomena occurring during the cycle of operation of an internal combustion engine and its application to the study of knock. Taylor (15) discusses the use of a rapid compression machine to study the time lag before spontaneous ignition occurs for fuel-air mixtures under conditions simulating end-zone gas conditions encountered in engines, which may lead to some data on chemical reaction kinetics. Perhaps the time is approaching when the great mass of data available in this entire field of knock-limited fuel performance in internal combustion engines can be correlated in terms of more fundamental factors.

**Antiknock agents** permit the use of higher compression ratios, more advanced spark, or increased supercharging, and therefore result in higher thermal efficiency in engines designed to take advantage of the decreased tendency to knock. It has been estimated that the improvement in engine efficiency made possible by the use of an antiknock agent to decrease tendency to knock saves over 50,000,000 bbl. of gasoline a year. Antiknock agents are those materials, such as gasoline-soluble compounds of lead, tin, titanium, selenium, tellurium, iron, nickel, and bismuth, which, when present in concentration of about 0.1%, exert catalytic control of certain of the chemical reactions in the end-zone gases that take place in an engine during the combustion of hydrocarbons, with resulting decreased tendency to knock. Boyd (3) gives a very interesting first-hand account of the early work in developing antiknock agents, including the many auxiliary problems that had to be solved before satisfactory status was attained for tetraethyl lead, making it the only highly successful commercial antiknock agent. Tetraethyl lead fluid (roughly two-thirds tetraethyl lead and one-third ethylene dibromide or other alkyl halide) is used in a very large percentage of all motor and aviation gasolines. The amounts of "fluid" used vary from 0.00 to over 2.0 ml. per U.S. gallon in "regular" automotive gasolines, 1.0 to 3.0 ml. in most "premium" ethyl automotive gasolines, and 3.0 to 4.0 ml. in most aviation gasolines. Thus, 0.00–0.113 vol. % of tetraethyl lead fluid is used in commercial gasolines. Approximately 300,000,000 lb. of tetraethyl lead was so used in the U.S. in 1950 (see *Lead, tetraethyl*).

The use of inorganic compounds or nonhydrocarbon fuels in internal combustion engines may raise very serious problems in engine design and materials of construction. As would be expected, the inclusion of lead compounds in gasoline led to the formation of solid products of combustion such as lead oxide. Since lead bromide is more volatile than lead oxide, it was found that use of ethylene dibromide in theoretical proportions with the lead aided markedly in scavenging the inorganic ash. The presence of bromine compounds tended to cause corrosion of the metallic engine parts, which

was avoided by the use of special alloy materials for valves, valve seats, etc., and by thermostatic control of the engine coolant system. Since bromine reacts with lead, it tends to deactivate the antiknock catalyst, but in the theoretical proportions this effect appears negligible. The demand for bromine for use in antiknock agent blends required the development of the process for the recovery of bromine from sea water to assure adequate supplies. Since the normal boiling point of ethylene dibromide is 228°F. and that of tetraethyl lead about 400°F., it would be expected that under conditions of incomplete evaporation of gasoline in the intake manifold of an engine the actual total concentration and the ratio of bromine to lead in some fractions of fuel-air mixture formed would vary appreciably from that in the original fuel. Such expectations have been confirmed experimentally, and in a few cases have caused serious trouble in engines. The effect appears aggravated by the inclusion of several per cent of fuel boiling at the same temperature as the tetraethyl lead. Aniline was one of the first antiknock agents known, and, during World War II, many other aromatic amines were investigated. The mechanism of the antiknock action of amines appears to differ from that of the metallic antiknock agents, and larger quantities are required which leads to its own set of serious problems in engine design and operation. Water injection was used extensively in aircraft engines during World War II to decrease the tendency to knock, thus permitting increased power, and to supply the internal cooling thereby necessitated. It appears that the cooling of the end-zone gases is the predominant cause of the decreased tendency to knock with water or water alcohol injection.

### Diesel Cycle Engines

**Physical and Chemical Delay Factors in Combustion.** In contrast to the relatively homogeneous mixture of fuel and air which is charged to the Otto cycle gasoline engine, the Diesel engine charges air and compresses it during the intake and compression strokes of the cycle, and then liquid fuel is introduced as a jet or atomized spray into the compressed air. The mixing and combustion of this heterogeneous mixture must be completed in a very short time. Pressure-time curves from engines, such as shown by Taylor (14), show that combustion in Diesel engines occurs in three phases. First there is an appreciable delay between the start of the fuel injection and the time at which ignition is indicated by a rapid increase in the rate of rise of the pressure-time curve. The second phase, of very rapid combustion, seems to be due to spontaneous ignition occurring nearly simultaneously in many very small sections (microsections) of the heterogeneous fuel-air mixture. The third phase, of slower combustion, is limited by the availability of oxygen to the still unburned fuel and is controlled largely by the duration of the fuel injection, the rate of mixing of fuel and air, and the overall fuel-oxygen ratio existing in the combustion chamber during this phase. These three phases have also been observed directly in high-speed motion pictures of combustion in Diesel engines.

The delay period is affected by physical factors, such as the size of liquid fuel droplets, their velocity relative to the air, the volatility and viscosity of the fuel, the volume of air for complete combustion required per volume of liquid hydrocarbon, and by chemical factors, such as mechanism of autoignition of hydrocarbons, chemical composition, and kinetics of chemical reactions occurring during the delay period which involves energy of activation, temperature, pressure, and fuel-air ratio. It should be

remembered that the actual fuel-air mixture during the delay period is very heterogeneous. Atomization, vaporization, and mixing are all occurring simultaneously, so the combustion chamber contains liquid fuel in various stages of subdivision mixed and unmixed with air, and fuel vapor mixed and unmixed with air. Ignition can only occur in those microsections, consisting of fuel-air mixtures within the flammability limits, that are at a temperature at or above the corresponding spontaneous ignition temperature, and in which the preflame chemical reactions have occurred to some definite stage. Elliott (6) discusses in considerable detail the fundamental principles underlying the physical and chemical factors controlling the three stages of combustion.

The fundamental chemical principles involved in Diesel engine combustion are similar to those involved in Otto engine combustion with emphasis on chemical reaction kinetics preceding spontaneous combustion, although the types of combustion desired for smooth operation of the two types of engines are nearly opposites. For Otto cycle gasoline engines, high octane number fuels are preferred because they have long chemical delay characteristics which permit the normal flame front to reach all portions of the combustion chamber before the chemical kinetics of the fuel-air mixture in the end zone reach a stage where spontaneous ignition occurs. For Diesel engines, fuels are preferred that have very short chemical delay characteristics, so as to provide early ignition upon injection into the compressed air in the combustion chamber, thus giving good control of the combustion process in the very heterogeneous fuel-air mixture that must be handled. Diesel fuels are rated according to their "cetane number" (see below). As would be expected, the effects of chemical composition, molecular structure, etc. upon cetane number are approximately the opposite of their effects upon octane number.

**Engine Performance Tests.** Extensive Diesel engine fuel performance tests have been conducted to determine the effects of fuel characteristics upon starting, smoothness, smoke, exhaust odor, power, fuel consumption, and combustion chamber deposits. Increased cetane number has been shown to have a direct relation to improved starting, improved smoothness, and decreased misfiring and combustion chamber deposits. No direct relation to power or fuel consumption was reported (in contrast to the octane number in Otto cycle engines). Decreased volatility, as indicated by an increased 90% distilled temperature in the A.S.T.M. distillation, tends to increase smoke and deposits, but has little effect upon the other performance factors. An increased carbon residue on the 10% bottoms from the A.S.T.M. distillation also tends to increase smoke and deposits. Table II indicates the limits set for some of the specification tests of the A.S.T.M.

TABLE II. Specification Test Limits for Three Typical Diesel Fuel Oils.

Grade	Flash point, °F. <sup>a</sup>	Carbon residue, % of 10% <sup>b</sup>	Ash, wt. % <sup>b</sup>	Distillation temp., °F. <sup>b</sup>		Viscosity at 100°F., S.U.S. <sup>c</sup>		Sulfur, wt. % <sup>b</sup>	Cetane no. <sup>d</sup>
				90% pt.	End pt.	Min.	Max.		
1-D	100	0.15	0.01	—	625	1.4 <sup>a</sup>	—	0.50	40
2-D	100	0.35	0.02	675	—	—	45	1.00	40
4-D	130	—	0.10	—	—	45	125	2.00	25

<sup>a</sup> Minimum limit.

<sup>b</sup> Maximum limit.

<sup>c</sup> Saybolt Universal seconds.

<sup>d</sup> Centistokes.

Source: A.S.T.M. Tentative Specifications for Diesel Fuel Oils (D975-48T).

The A.S.T.M. (1) has published a tentative method of engine test for ignition quality of Diesel fuels by the cetane method (D613-48T) which uses cetane and 1-methylnaphthalene as primary reference fuels to evaluate the ignition quality by a bracketing procedure similar to that used in determining octane number with reference fuels. The method evaluates a fuel by measuring the compression ratio (of the variable compression ratio test engine) at which the ignition delay period is 13 degrees of crankshaft travel, under very carefully specified standard operating conditions, and converting to cetane numbers by measuring the compression ratio for the bracketing reference fuels when their ignition delay period is also 13 degrees. The C.R.C. handbook (5) outlines research procedures for fuel tests in full-scale Diesel engines (C.R.C. Designation F-18-545) to test the relation between fuel characteristics and engine fouling, power and economy, smoke, cold starting, roughness and knock, and odor and lacrimation.

**Chemical Composition and Performance.** The chemical composition of Diesel fuels is very complex since they may contain any hydrocarbon of from 10 to 20 carbon atoms, including paraffins, naphthenes, and aromatics, and hydrocarbons whose molecules belong, in part, to two or three of these families. Smith (13) gives a comparison of the chemical compositions of a straight-run and of a catalytically cracked Diesel fuel which is of aid in general orientation in this field. Obviously it is a far cry from the thoroughness of this type of attack in the field of gasolines to the lack of detailed information on chemical composition and the performance of pure hydrocarbons in the field of Diesel fuels. Since 1907, many attempts have been made to obtain simple physicochemical laboratory tests or criteria to correlate with Diesel fuel performance tests. Specific gravity, boiling point, viscosity, aniline point (minimum equilibrium solution temperature of equal volumes of aniline and the sample), specific dispersion, parachor, and ring analysis have been used and are of some value. In general, several of these factors are interrelated, hence various combinations would be expected to give reasonable correlations regarding chemical composition and fuel performance. Mid-boiling point versus A.P.I. gravity, and the *Diesel index* (A.P.I. gravity times the aniline point, A.S.T.M. D611-47T, divided by 100) give some correlation with cetane number as determined by the engine ignition quality test. However, such empirical correlations may be very misleading in investigating the effect of additives such as alkyl nitrites for improving cetane number or starting characteristics. Since the demand for Diesel fuel has been increasing at a very rapid rate the general relationships between fuel performance in engines, and fuel availability as affected by chemical composition, crude oil sources, and refining technology may be expected to require increased cooperative research and development effort by all concerned.

### Gas Turbine Engines

The steady-flow, constant-pressure cycle used in gas turbine engines permits the use of separate equipment for: (1) compressing the gas streams, (2) carrying out the combustion process, and (3) developing power by the gas turbine. It is therefore possible to design combustion units to handle available fuels of any type varying from high-ash coal, residual fuel oil, distillate fuel oil, kerosene, and gasoline to gaseous fuels, largely independent of the compressor and turbine. While it may appear exaggerated to consider the regeneration unit of a petroleum catalytic-cracking unit or a gas producer operating on coal as an integral part of the combustion unit of an internal com-

bustion gas turbine engine, such considerations may have important commercial applications. However, most internal combustion engines have found greatest utility in mobile power uses and use liquid petroleum fuels to obtain very high heat release rates in relatively small combustion units, so the discussion of fuel performance factors will be restricted to liquid fuels.

The combustion process in internal combustion gas turbines is somewhat similar to that occurring in Diesel engines, in that a liquid fuel is atomized into a body of air, and combustion is sustained by spontaneous ignition. The cycle is a continuous one, involving: (1) compressing the inlet air by centrifugal or axial flow compressors equivalent to a compression ratio of from two to four or more; (2) injecting the fuel into a portion of the air stream to obtain vaporization and the formation of fuel-air mixtures within the flammable limits, and burning part of the fuel; then (3) gradually adding sufficient excess air to decrease the temperature of the combustion gases to 1500°F. or below, as dictated by the maximum permissible temperature limits of the gas turbine blades. The combustion phase is characterized by a heterogeneous mixture of liquid fuel, fuel vapor, fuel-air mixtures, excess air, and combustion products, quite analogous to the Diesel engine except for the lower temperatures, pressures, overall fuel-air ratios, and higher air velocities encountered in the gas turbine engine.

Lloyd (9) summarizes current data available on this problem, and points out that viscosity, initial and final volatility, elementary carbon, hydrogen, oxygen, and sulfur analysis of the organic constituents, and the physical characteristics of the ash appear the most helpful laboratory tests, and that the A.S.T.M. standard tests for flash point, carbon residue, distillation, etc., should also be useful. The significance of such tests must be determined by gas turbine engine performance tests, hence close cooperation between engine designers and manufacturers and fuel manufacturers appears to be essential here, as was the case in the development of fuels for Otto and Diesel cycle engines. Viscosity has a marked influence upon the effectiveness of atomization in the pressure-type nozzles usually used in gas turbine engines. The viscosity, and the volume of air required per volume of liquid fuel for stoichiometric mixtures, both increase with an increase in molecular weight of the fuel, whereas volatility decreases with an increase in molecular weight. These factors, thus, increase the severity of the combustion conditions. The tendency to form smoke and carbon deposits in the combustion chamber liner increases as the C/H ratio of the fuel increases. Ignition delay has been shown to correlate with chemical composition in Otto and Diesel engines, and somewhat similar effects have been reported for gas turbine combustion. However, at the high temperatures encountered in the combustion process in gas turbine combustion, fuel performance does not appear to vary markedly with chemical composition, except for the effect of C/H ratio. Due to the high temperatures encountered and the heterogeneous mixture present, some thermal cracking of the fuel has been reported to occur in the liquid droplets and also in the fuel-rich vapors surrounding the droplets.

No fuel performance criteria for gas turbine fuels dependent directly upon chemical composition that definitely limit engine design for more power or more economy, comparable to knock limitations of Otto cycle engines, have been definitely demonstrated. Gas turbine engines appear most promising for high-power installations in contrast to the Otto cycle gasoline engine which has found greatest utility in automobiles. Low cost and readily available fuels appear to be essential, if the gas turbine is to develop a large field in competition with other types of prime movers.



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G. G. LAMB

## JET PROPULSION FUELS

In air-breathing aircraft jet engines, the fuel is burned with oxygen from the air, as contrasted with rockets, which carry their own oxidant (see *Rocket propellants*). Jet engines can be divided into three types: the ram-jet, the turbo-jet, and the pulse-jet. See Figure 1. In all three types, propulsion is obtained by reaction by emitting the

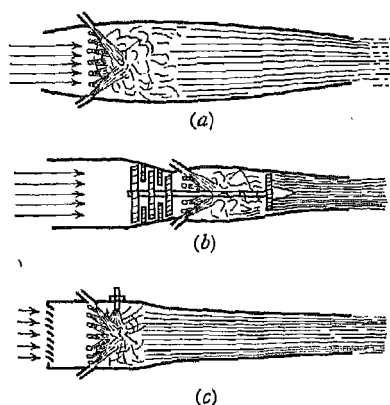


Fig. 1. Three types of jet propulsion engines: (a) ram-jet, (b) turbo-jet, (c) pulse-jet (4).

exhaust gases backward at a high velocity. They differ in the manner in which the combustion air is compressed. In the ram-jet, compression is obtained by "ram" alone (that is, from the velocity of the aircraft itself). In the turbo-jet, the exhaust gases drive a turbine which provides sufficient power for compressing the air. In the pulse-jet (which was used in World War II in the German V-1 or "buzz bomb"), the admission of air is intermittent, controlled by a set of movable louvers. In the turbo-jet, it is possible to generate sufficient power to drive a propeller (turbo-prop), or the same principle may be applied to yield all the power from the turbine, giving the gas turbine engine (see *Fuels, internal combustion*).

The ram-jet and the pulse-jet are, at the present time, visualized as being primarily suited for specialized military uses. The ram-jet seems best suited as a supersonic power plant since at lower speeds the turbo-jet is more efficient and is capable of developing high thrust under take-off conditions, while the ram-jet must be accelerated by some means other than its own power. The pulse-jet, which seems best suited as a cheap, expendable, power plant for subsonic flight conditions, can develop useful thrust under take-off conditions but is not as generally useful an aircraft power plant as the turbo-jet. While the fuel requirements for the ram-jet and the pulse-jet are basically

similar to the turbo-jet, details regarding fuel problems in these two engines are primarily a matter of military interest and are not available for publication.

The problem of fuel selection for turbo-jet type engines has been the subject of considerable interest in recent years because of the potentially large quantities of fuel which will probably be required by this type of engine. For military applications it has almost entirely displaced the reciprocating engine in fighter planes and high-speed bombers, and it is expected that the turbo-jet and turbo-prop motors will be rather extensively used in commercial airlines in the future, although their use is, at present, confined to a few experimental models.

Potential fuels for jet engines can be judged primarily on their heat of combustion, ease of combustion, handling characteristics, and cost and availability. Hydrocarbons derived from petroleum are without serious competition when all of these factors are considered. A few metallic and organo-metallic substances have higher heats of combustion but are at a disadvantage when cost and availability and the other factors are taken into consideration. While such fuels may have a few special applications, petroleum hydrocarbons can be considered as the major jet fuel.

Table I summarizes some of the properties of interest for a number of petroleum hydrocarbon fuels ranging in volatility from pentane to heavy fuel oil. In this table, the heats of combustion, relative to kerosene, are given on both a weight and volume basis. It is obviously important to keep both weight and volume of the fuel as low as possible, since increasing either the weight or the volume of aircraft increases the power required to fly at a given speed. The relative importance of fuel weight and volume depends on the specific application, but, in general, weight is the more important consideration in low-speed aircraft because sufficient fuel storage volume is frequently available, while volume is the more important consideration in high-speed aircraft, since fuel storage volume is frequently limiting. It is seen in Table I that the volatile hydrocarbons excel on a weight basis, but that the high-molecular-weight hydrocarbons are to be preferred on a volume basis. Since jet engines are most commonly used in high-speed aircraft, the tendency would be to use the higher-molecular-weight fuels in order to obtain maximum range in a given airplane; however, since the difference in heat of combustion between the various fuels is not very large, a number of other factors are given equal or greater weight in setting up fuel specifications.

TABLE I. Properties of Petroleum Fuels for Turbo-Jets.

Fuel	Relative heat of combustion per unit weight	Relative heat of combustion per unit volume	Initial b.p., °F.	Mid-b.p., °F.	F.p., °F.
Pentane.....	1.05	0.80	97	97	< -76
Heptane.....	1.03	0.87	209	209	< -76
MIL-F-5624 (JP-3).....	1.01	0.97	116	390	< -76
MIL-F-5616 (JP-1 kerosene)....	1.00	1.00	320	385	< -76
Diesel fuel.....	0.99	1.01	388	508	0
Heavy fuel oil.....	0.95	1.15	—	—	10

It is desirable that the combustor in a jet engine burn the fuel efficiently over all operating conditions encountered by the aircraft using the engine. The rate at which a fuel-air mixture can be burned, under the turbulent flow conditions encountered in a jet engine combustor, decreases as pressure and temperature are decreased. It is

therefore necessary to design the combustor for the highest altitude and lowest compression-ratio conditions that are expected in use. A combustor that is satisfactory under severe conditions is generally highly efficient under sea-level operating conditions, so that any effect of fuel composition on efficiency is usually observed only under high-altitude operating conditions. The ease of burning, besides depending on pressure and temperature, depends on the chemical composition of the fuel. Highly unsaturated hydrocarbons burn more easily than aromatics and saturated hydrocarbons, but, within the limitation of cost and availability imposed on jet fuels, there is not enough difference between the various hydrocarbons in ease of combustion to make the matter of great interest.

In order for the fuel to burn, it must first be vaporized and mixed with the air. It is found that the vapor pressure of the fuel, the fineness of atomization, and the flow pattern in the combustor all have a pronounced effect on performance under high-altitude operating conditions. Figure 2 shows efficiency as a function of temperature rise of the air, due to combustion, for two fuels and two pressures (1). The reduction

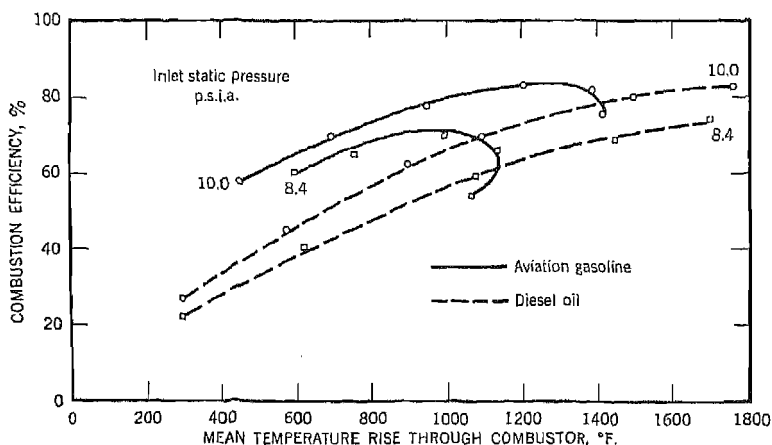


Fig. 2. Variation of combustion efficiency with mean temperature rise (inlet temperature, 240°F.; inlet velocity, 200 ft./sec.) (1).

of combustion efficiency by lowering pressure is illustrated for both fuels, and it is noted that at lean mixture (lower temperature rise) higher efficiency is obtained with the more volatile aviation gasoline. As fuel rate is increased, to give a higher temperature rise, better results are obtained with the Diesel fuel, and a temperature rise limitation is noted with the aviation gasoline. With other combustor designs and at other operating conditions, quite differently shaped curves might be found, and it is difficult to generalize on the exact effect of changing fuel volatility or quality of atomization on altitude efficiency. In general, however, with a properly designed combustor, it should be possible to obtain best efficiency with the more volatile fuels and, at the same time, obtain a sufficiently wide range of temperature rise, although with many designs there are more severe temperature rise limits with the more volatile fuels. In order to take advantage of this potentially improved performance with increased fuel volatility, some combustion chamber designs use fuel vaporizers, instead of injecting through an atomizing nozzle as is more commonly done. While fuel volatility may have an important effect on operation under limiting conditions, the effect of volatility on altitude operation is not generally considered an important factor in the choice of

a fuel for the turbo-jet engine since more weight is given to considerations concerning supply, safety, and evaporation losses. This attitude has been made reasonable by the ability of the engine manufacturers to develop engines capable of burning the fuel supplied under the necessary operating conditions.

While efficiency and range of temperature rise are generally satisfactory under low- and moderate-altitude conditions, it has been found that many fuels have a tendency to deposit carbon on the inside of the combustor where it may interfere with the operation of the spark and the fuel atomizing nozzle and may contribute to the warping of the combustion chamber by causing uneven heating.

As illustrated in Table II, the amount of carbon deposited in a combustor increases with increasing boiling point of the fuel or with increasing aromatic content (1).

TABLE II.

Fuel	B.p., °F.	Aromatics, %	Carbon deposit, grams
Isoheptane.....	182	0	2
Benzene.....	172	100	30
Ethylbenzene.....	271	100	45

The National Advisory Committee for Aeronautics has correlated the carbon-forming tendencies of fuel with the C/H ratio of the fuel, the tendency to form carbon decreasing with decreasing C/H ratio. This is in accord with the previously shown data, since the C/H ratio is higher for aromatics than for paraffins, and the C/H ratio increases as the boiling point of the fuel increases.

Quantitative study of carbon formation has been made difficult by the extreme sensitivity of this behavior to small changes in physical configuration of the combustor. In one engine, using 14 combustors, it was found that, after a run under controlled conditions, the amount of carbon varied by a factor of two between various combustors, while, with another engine, a factor of 13 between different combustors was observed. If a single combustor is taken from an engine and repeated runs are made under identical conditions, a difference of 50% between runs is commonly observed. More consistent results are obtained with research combustors that are dimensionally more stable, and some thought has been given to standardization on a particular combustor design for evaluation of the carbon-forming tendencies of fuels.

In practice, the carbon-forming tendencies of a fuel are controlled by specifying an allowable percentage by volume of aromatics and the final boiling point of the fuel, although this latter specification is also determined by consideration of supply and freezing point. It is apparent that, if the aromatics are concentrated in the lower-boiling portions of the fuel, there will be less of a tendency to form carbon than if they are concentrated in the high-boiling portions. As shown in Table III, the current specification for a military jet fuel used by the U.S. is 25% aromatics by volume. This is based on tests of fuels considered typical of what might be produced in large quantities.

In kerosene-type jet fuels, the specification is generally for 20% aromatics. A result of modern petroleum processing methods is to convert paraffinic and naphthenic compounds into aromatic ones, simultaneously reducing the molecular weight of the feed stock. Cracking is necessary in order to manufacture a maximum amount

of gasoline- and kerosene-type fuels; so, in order to assure maximum supply and minimum cost, it is desirable to allow a certain amount of aromatics in the fuel.

TABLE III. *Present Aviation Turbo-Jet Fuel Specifications.*

Specification	Limit	Type of fuel	
		Kerosene JP-1 (MIL-P-5616)	Wide-boiling JP-3 (MIL-P-5624)
Specific gravity (60/60°F.)	Max.	0.850	—
Reid vapor pressure, p.s.i.	Range	—	5-7
Flash point (Tag closed cup), °F.	Min.	110	—
A.S.T.M. distillation			
10% pt., °F.	Max.	410	—
90% pt., °F.		490 (max.)	400 (min.)
Final end pt., °F.	Max.	572	600
Residue, %	Max.	1.5	1.5
Loss, %	Max.	1.5	1.5
Freezing point, °F.	Max.	-76	-76
Corrosion test (212°F., 3 hr.)	Max.	Slight discoloration	
Sulfur, wt. %	Max.	0.20	0.50
Aromatics, vol. %	Max.	20	25
Bromine number, eq./100 g.	Max.	3	30
Viscosity at -40°F., centistokes.	Max.	10	—
Residue (400°F. air jet), mg./100 ml.	Max.	5.0	10
16-hour accelerated Army gum test, mg./100 ml.	Max.	8.0	20
Net heat of combustion, B.t.u./lb.	Min.	—	18,400
Inhibitor content, lb./5,000 gal.	Max.	—	1

In the choice of the vapor pressure allowable in a fuel, three major considerations have to be taken into account: (1) supply, (2) vaporization losses, and (3) safety. Ease of combustion as previously mentioned is a secondary consideration and is not given much weight.

For military aircraft, the problem of supply becomes of paramount importance. Estimates based on assumed wartime requirements for jet fuel indicate that a sufficient quantity of kerosene-type jet fuel could not be manufactured in time of emergency, but that it would be possible to meet the demands by including both higher and lower-molecular-weight materials than are included in kerosene-type fuels. A 5-7 lb. Reid vapor pressure has therefore been specified for JP-3, the military jet fuel, which gives it a volatility comparable to that of gasoline. This fuel has a maximum availability of approximately 50% of the crude run as compared to roughly 10% for a kerosene-type fuel.

If the fuel in the airplane has been warmed by standing in the sun, rather large losses of fuel due to vaporization can occur if the plane climbs rapidly to a high altitude. This loss, together with attendant difficulties of pumping fuels near their boiling point, is a serious disadvantage which might make it desirable to use a somewhat lower vapor pressure fuel.

The high-molecular-weight material that can be included in jet fuel is limited by freezing point since it is necessary to be able to pump the fuel through the lines, filters, and combustor spray nozzles. A freezing point specification of -76°F. has been set for U.S. military fuels. When volatile components are included in the fuel, it is also possible to include more high-molecular-weight components for a given freezing point.

It is therefore possible to include higher-molecular-weight material in the volatile JP-3 fuel than in kerosene-type fuels which further increases the portion of crude petroleum which can be included in jet fuel.

The corrosiveness and tendency to form high polymers (gum) are also controlled by specification. These requirements are based to a considerable extent on experience with fuels for reciprocating engines where the fuel is vaporized before entering the cylinders, and it is probable that different requirements will be found for jet fuels when further experience is gained.

Certain mixtures of petroleum hydrocarbon vapors and air are highly explosive and therefore constitute a safety hazard. Explosive mixtures are obtained over a range of temperature which depends on the total pressure and the volatility of the fuel. Such data are shown in Table IV for several fuels and altitudes.

TABLE IV.

Altitude, ft.	Explosive limits, °F.	
	JP-3 <sup>a</sup>	Kerosene <sup>b</sup>
0	-40 to +18	+95 to +170
20,000	-62 to -12	+70 to +135
40,000	-78 to -42	+48 to +95

<sup>a</sup> U.S. military jet fuel 7 lb. Reid vapor pressure.

<sup>b</sup> 0.15 lb. Reid vapor pressure.

It can be seen that the more volatile military jet fuel, except for winter conditions, has too rich a mixture in the vapor space to explode, but, if this rich mixture were to be diluted with the proper amount of air, it would be explosive and would therefore be considered more dangerous than the too lean mixture usually obtained with a kerosene-type fuel. This is borne out by operational experience which indicates that serious fires are much less likely to occur in mild airplane accidents if kerosene-type fuels rather than gasoline types or JP-3 are used. For severe crashes, fires are common with kerosene-type fuels; however, in this type of crash the occupants of the plane are generally killed as a direct result of the crash and the fire is not such an important consideration. Because of greater safety, it is expected that a kerosene-type fuel will be specified for civilian aircraft using jet engines for which a sufficient supply would probably be available at a reasonable cost.

The choice of fuel for a potentially large demand as appears to exist for jet fuels is a delicate balance between small gains in performance of the engine and cost and availability of the fuel. As economic and technological factors vary with time it is to be expected that fuel specifications will undergo further change to maintain the optimum balance between performance and supply.

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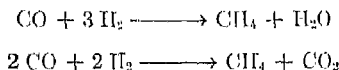
## FUELS, SYNTHETIC LIQUID

In the year 1902, the French scientists Sabatier and Senderens first reported the synthesis of a hydrocarbon by the catalytic reduction of carbon monoxide and hydrogen. In 1950, a full-scale plant, utilizing a modification of this classical reaction, was ready to produce commercial quantities of synthetic gasoline and other hydrocarbon oils to sell competitively with similar products derived from natural petroleum. Between these two incidents lies a story of development which in the expenditure of manpower and money has seldom been equaled by private industry.

Credit for producing the first traces of hydrocarbons and carrying on the development to the erection of full-scale plants in Germany before World War II belongs to Franz Fischer and his co-workers at the Kaiser Wilhelm Institut für Kohlenforschung, Mülheim, Germany. Postwar activity aimed at the development of processes for the production of fuels competitive with those derived from natural petroleum has been centered in the United States. A number of petroleum engineering and refining interests, including most of the major oil companies, have been active in this field. The first such process to be reduced to practice was the Hydrocol process, a development of Hydrocarbon Research, Inc., who designed the first full-scale plant erected for Carthage Hydrocol, Inc., at Brownsville, Texas. The names "Synthol" and "Synthine" have been used at times to designate similar processes. The production of predominantly oxygenated compounds by the catalytic reduction of carbon monoxide with hydrogen is discussed under *Oxo and oxyl processes*. See also *Hydrogenation*; *Methanol*.

## Historical Review

Sabatier succeeded only in producing the simplest hydrocarbon, methane, by passing hydrogen and carbon monoxide over nickel and cobalt catalysts at atmospheric pressure:

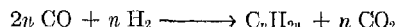


**High-Pressure Synthesis.** In 1913, Badische Anilin- & Soda-Fabrik patented the possibility of producing mixtures of higher hydrocarbons and other chemicals, such as alcohols, aldehydes, ketones, and fatty acids, by the reduction of carbon monoxide with hydrogen. The synthesis described in this patent differed from the work of Sabatier chiefly in that it was to be carried out at pressures above 100 atm. Operating conditions were defined in the broadest terms and catalysts included, among others, nickel, cobalt, iron, manganese, chromium, titanium, osmium, palladium, and zinc. There is no account in the literature of higher hydrocarbons actually having been synthesized by the method described. On the other hand, the production of oxygen-containing compounds by the high-pressure synthesis was reduced to practice. In 1923, two such processes were disclosed.

In 1923, Badische Anilin- & Soda-Fabrik announced the successful development of the controlled catalytic conversion of carbon monoxide and hydrogen to methanol to the exclusion of other products (71,72). This process has been widely used both in Europe and in the U.S. It is carried out at even higher pressures and at somewhat lower temperatures than most of the earlier work, that is, 200–300 atm. and 300–400 °C. In the same year, Franz Fischer and Hans Tropsch announced their Synthol process (25). Using alkalized iron filings as a catalyst, they were able to effect the reduction of carbon monoxide with hydrogen to produce a mixture of alcohols, aldehydes, ketones, and fatty acids (18).

**Fischer-Tropsch Normal-Pressure Synthesis.** In 1926, Fischer and Tropsch published their classical work on what they termed the normal-pressure synthesis as distinguished from the earlier high-pressure investigations (26). In this publication, they described, in some detail, conditions for the production of predominantly higher hydrocarbons. The reaction carried out in this general manner has since been referred to as the "Fischer-Tropsch synthesis." It was carried out at atmos-

pheric pressure and at a temperature below the level at which methane is formed. Hydrocarbons were produced by net reactions similar to those observed by Sabatier:



It is interesting to note that after much experimentation at increasingly higher pressures, Fischer and Tropsch went back to atmospheric pressure where Sabatier had started. They had, however, learned to avoid the high temperatures at which methane formation is predominant, and had been able to do so by developing more active catalysts. They had also learned to use catalysts with small concentrations of alkali to increase the average size of the hydrocarbon molecule.

One year after Fischer and Tropsch described the normal-pressure synthesis, a small pilot plant was built and operated at the Kaiser Wilhelm Institut. By this time the yield of liquid hydrocarbons using both iron and cobalt catalysts (Fe:Cu (4:1), 0.2%  $\text{K}_2\text{CO}_3$ , and Co:Cu (9:1), no alkali) had been increased to 20–25 cu.cm. per cubic meter of water gas, still far from an attractive commercial yield, but a long stride forward from the trace yields of 1923–26. The output per unit volume of reactor had likewise been markedly increased, but at 5 cu.cm. of liquid product per hour per liter of reactor volume, it too was far from attractive commercially.

By 1930, Fischer, Meyer, and Koch had developed the technique of dispersing the catalytically active metals on carriers, thereby making much less dense catalysts (28). This was accomplished by decomposing the appropriate nitrates in the presence of porous carriers. A cobalt catalyst so prepared quadrupled the yield of liquid hydrocarbons and approximately doubled the reactor output. Even higher yields were attainable by recycling the gas, but recycling was not attractive at atmospheric pressure because of the large volumes of gas involved.

In 1931, Fischer and Meyer prepared a catalyst by precipitating nickel on kieselguhr in the presence of thorium as an activator (21). By carefully controlling the reduction of the catalyst, yields up to 120 cu.cm. of liquid hydrocarbons per cubic meter of water gas were obtained. The best catalyst of this type had the general formula: Ni:ThO<sub>2</sub>:kieselguhr, 100:18:100. Cobalt catalysts of the same general formula but superior to the nickel catalysts were developed during the following year by Fischer and Koch, and gave yields of liquid hydrocarbons up to 150 cu.cm. per cubic meter of water gas (20).

The next step of importance in the commercial development of the Fischer-Tropsch synthesis was not an improvement of the synthesis proper, but a process for purification of water gas. It was an easy matter to obtain the desired 2:1 hydrogen to carbon monoxide ratio by converting part of the carbon monoxide with steam to carbon dioxide and water over a catalyst. However, the water gas invariably contained organic sulfur which rapidly poisoned the synthesis catalysts. "Luxmasse" (hydrated iron oxide) had been used for years to remove hydrogen sulfide, but it does not remove organic sulfur.

A process for removal of organic sulfur was developed by Roelen and Feisst in 1933 (73). The water gas was first freed of hydrogen sulfide by the conventional iron oxide process, and the residual gas was then passed over highly alkalized iron oxide at 200–300°C. Under these conditions, the organic sulfur reacts with hydrogen to form hydrogen sulfide, which is absorbed by the iron oxide. The gas so purified contains less than 1 grain of sulfur per 1000 cu.ft.

When the Fischer-Tropsch synthesis showed promise of being of commercial value under the controlled economy of Germany, Ruhrchemie, a company owned by a number of mining interests of the Ruhr district, purchased operating and licensing rights for the process from the Kaiser Wilhelm Institut, and in 1934 erected a 25-bbl.-per-day semicommercial plant at Oberhausen-Holtien and operated it successfully. In the following year, Ruhrchemie built a full-scale plant at Oberhausen-Holtien. Over the course of the next few years, five additional normal-pressure plants were erected in Germany.

In 1935, Fischer and Pichler carried out the synthesis in steps, with removal of water and condensable hydrocarbons after each step (22). Conversion in the first step was limited by the use of a less active catalyst. The yield of liquid per unit of synthesis gas was increased to 141 grams per cubic meter, and the output per unit of reactor volume was increased 10–20%. Also, by using in the first stage the spent catalyst from the second or third stage, the overall life of the catalyst was increased. Once this type of operation had been proved successful by Ruhrchemie at Oberhausen-Holtien, all commercial plants were converted to it.



Although full-scale plants were built and operated successfully, there was one serious technical defect in the normal synthesis process. It was necessary to interrupt the operation and treat the catalyst with hydrogen every 3-6 weeks to remove the high-molecular products. It was also necessary to replace the catalyst on the average of every 4-8 months, depending on the amount of sulfur in the gas and the care with which the synthesis was controlled. The metal was recovered from the spent catalyst and re-used, but reworking was expensive.

**Fischer-Pichler Medium-Pressure Synthesis.** In 1936, Fischer and Pichler described the medium-pressure synthesis with cobalt catalysts at 5-20 atm. (24). The yields of hydrocarbons were 10-15% higher than by the normal-pressure synthesis. There was a very definite optimum pressure range. The process had several remarkable advantages over the original Fischer-Tropsch synthesis. The yield of paraffin wax, a very valuable product to the Germans at the time, could be increased from 10 to 45% of the liquid product. The periodic treatment of the catalyst with hydrogen was not necessary. The life of the catalyst was increased to one year or longer. The reactor output was increased 10-20%, and the benefits of recycling gas could be obtained at far less expense than in the normal-pressure synthesis. The important difference between the Fischer-Pichler synthesis and

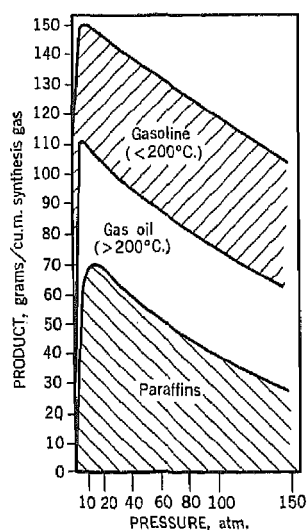


Fig. 1. Influence of pressure on yields of gasoline, gas oil, and paraffin (cobalt catalyst).

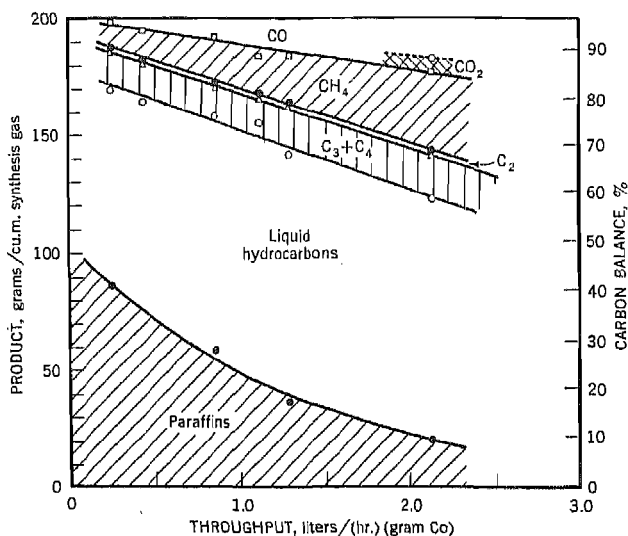


Fig. 2. Yields and carbon balances at different gas throughputs for medium-pressure synthesis (cobalt catalyst).

earlier superatmospheric-pressure experiments was the nature of the catalyst, which was not bulk metal but cobalt dispersed on kieselguhr.

Ruhrchemie promptly installed a medium-pressure converter at Oberhausen-Holtien, and it proved so successful that further plants were built for pressure operation. Some of the medium-pressure plants were converted to recycle operation (Lurgi, Ruhrchemie), and others were scheduled for conversion at the end of World War II, but the percentage of the total Fischer products made by this method was small.

Since the medium-pressure synthesis was the last improvement embodied in the Ruhrchemie plants, what it accomplished with respect to yields is of historic significance. This is shown in Figures 1 and 2. Figure 1 clearly shows the optimum yield of liquid hydrocarbons in the range of 10-20 atm. As the pressure is increased from normal pressure to the optimum, the product becomes progressively higher in molecular weight, the yield of gasoline decreases, and the yield of paraffins increases. Beyond the optimum pressure, the yield of paraffin decreases steadily with increasing pressure with little change in yield of gasoline and gas oil.

Figure 2 shows optimum yields of hydrocarbons obtained at different reactor throughputs. The optimum temperatures are 175-78°C. for a reactor throughput of 0.1 liter per hour per gram of cobalt,

180–92° for a throughput of 1, and 212–14° for a throughput of 2. As the gas rate to the reactor is increased, a marked decrease in total yield of useful products per volume of synthesis gas is observed; for example, there is a 20% decrease as the throughput is doubled from 1 to 2 volumes of gas per hour per gram of cobalt (100–200 volumes of gas per hour per volume of catalyst). This is of great significance because one of the factors that made the synthetic product expensive was the low reactor output. Commercial operations were conducted at approximately 100 volumes of gas per hour per volume of catalyst.

In 1937, Fischer and Pichler discovered that certain precipitated iron catalysts under certain circumstances could be used successfully at 10–30 atm. The yields obtained were increased from 50–60 grams per cubic meter of synthesis gas at atmospheric pressure to 150–160 grams at the higher pressure, and the lifetime of iron catalysts was increased from 4–6 weeks to several years (at a space velocity of 100 volumes of synthesis gas per volume of catalyst per hour). All results of the medium-pressure iron synthesis were obtained in the laboratory and in pilot plants; it was never tried on a commercial scale. Table I shows experimental results with precipitated iron catalysts, containing no metals other than iron and alkali. The precipitation of the iron catalyst was carried out similarly to the precipitation of cobalt catalysts, from dilute solutions of iron and alkali at 70–100°C. The precipitate is washed with distilled water and then impregnated with controlled amounts of alkali dissolved in water. The pretreatment (reduction and carbiding) has an important effect on the behavior of the iron catalysts during the synthesis.

Nine plants were operated in Germany. Five used the normal-pressure synthesis, two the medium-pressure synthesis, and two had converters of both types. All used cobalt catalyst exclusively. The larger plants had capacities of about 2,500 bbl. per day of liquid product. The production of the nine plants reached a high of 15–18,000 bbl. per day during World War II.

See also references (23,67a).

TABLE I. Yields Obtained with Iron Catalysts Containing Different Amounts of Alkali.<sup>a</sup>

Precipitant	K <sub>2</sub> CO <sub>3</sub> added, %	Total yield, g./cu.m. ideal gas	Composition of yield, %		
			Paraffin	Liquid hydrocarbons	C <sub>3</sub> –C <sub>4</sub> hydrocarbons
NH <sub>3</sub>	0	141	12	67	21
Na <sub>2</sub> CO <sub>3</sub>	0	140	13	67	20
None	0.25	148	26	56	18
Na <sub>2</sub> CO <sub>3</sub>	1	157	42	47	11
Na <sub>2</sub> CO <sub>3</sub>	5	155	46	44	10

<sup>a</sup> At 15 atm.; 230°C.; ratio of carbon monoxide to hydrogen, 3:2; single stage; no recycle.

**Properties of Fischer Liquid and End Uses.** Compared with natural petroleum, Fischer liquid from cobalt catalysts is the equivalent of a very paraffinic crude oil, but it is not as complex a mixture as natural petroleum, so that it is more valuable than petroleum for certain chemical uses. The molecules are predominantly straight-chain aliphatic and predominantly saturated, but there is an appreciable concentration of monoolefins. Alcohols, fatty acids, etc. are also present, but in very low concentrations, less than 1% of the total product.

The normal-pressure synthesis gives approximately 60% gasoline, 30% gas oil, and 10% paraffin (m.p. 20–100°C.); and the medium-pressure synthesis, 35% gasoline, 35% gas oil, and 30% paraffin. The octane number of the gasoline is too low for use directly as motor fuel (50–60). Most of the German production was blended with high-octane gasoline or with benzene from the coke ovens of the Ruhr district and sold as motor fuel. The gas oil was an excellent Diesel fuel; the greater part of the German production was used for this purpose. Some was used to make liquid soap (by sulfochlorination of saturated hydrocarbons—see *Surface-active agents*). The paraffin (sometimes referred to as “Gatsch”) was used primarily for the synthesis of

fatty acids (*q.v.*) for subsequent conversion to hard soaps and for other chemical uses. The propane and butane gas was used as an ersatz motor fuel, and in some instances the propylenes and butylenes were polymerized over phosphoric acid to produce high-octane gasoline. In certain plants, synthetic olefins were polymerized to lubricating oils.

**Development of Related Hydrocarbon Syntheses in Germany.** In 1938, Pichler announced the synthesis of very high-melting waxes (52a). Using a ruthenium catalyst and pressures of 100–1,000 atm., it was possible to produce waxes with molecular weights up to 23,000 and melting points up to 135°C. Such paraffins are unknown in nature. Properties of separate fractions of the crude product are shown in Table II. Over 50% of the product melts above 93°C.

TABLE II. Properties of Paraffins Obtained by High-Pressure, Low-Temperature Synthesis (Ruthenium Catalyst).

Fraction	Solvent	Extraction temp., °C.	Amt. dissolved, % of crude product	Melting range, °C.	Density at:		Mol. wt. (av.)	Viscosity, centistokes, at:	
					20°C.	150°C.		150°C.	180°C.
1	<i>n</i> -Pentane	34	30–33	51–57	—	—	—	—	—
2	<i>n</i> -Hexane	68	14–17	92.5–95	—	0.7654	760	6.06	4.0
3	Synthetic gas oil	90	14–16	121–22.5	0.966	0.7779	1,750	28.6	16.6
4	<i>n</i> -Heptane	98	20–25	129.5–30.4	0.978	0.7827	6,800	870	410
5	Synthetic gas oil	121	12–15	132–34	0.980	0.7859	23,000	35,600	15,800

Source: reference (54a).

In 1939, Pichler and Ziesecke developed the "isosynthesis" process (56). At high pressures and temperatures, using thoria and also mixtures of alumina and zinc oxide as catalysts, low-molecular isoparaffins such as isobutane and isopentane were synthesized from water gas. Yields up to 85 grams of isobutane plus 25 grams of higher isoparaffins were obtained. Typical results are shown in Table III.

TABLE III. Yields of Isosyntheses.\*

Catalyst	CO conversion, vol. %	Liquid hydrocarbons	Yield, g./cu.m. of synthesis mixture						
			Alcohols in:		Gaseous hydrocarbons:				
			Oil	Water	iso-C <sub>4</sub>	<i>n</i> -C <sub>4</sub>	C <sub>3</sub>	C <sub>2</sub>	C <sub>1</sub>
Al <sub>2</sub> O <sub>3</sub> (from aluminate)	24	14	0.7	—	10	6	4	0	9
ThO <sub>2</sub>	62	42	9	11	23	3	11	4	11
ThO <sub>2</sub> + 20% Al <sub>2</sub> O <sub>3</sub>	73	34	1	2	61	9	9	10	15
ThO <sub>2</sub> + 0.6% K <sub>2</sub> CO <sub>3</sub> + 20% Al <sub>2</sub> O <sub>3</sub> (based on ThO <sub>2</sub> )	70	42	2	4	51	7	18	6	12
ThO <sub>2</sub> + 20% Al <sub>2</sub> O <sub>3</sub> + 3% K <sub>2</sub> CO <sub>3</sub> (based on Al <sub>2</sub> O <sub>3</sub> )	78	25	0	0	85	10	0	7	22

\* At 300 atm.; 450°C.

Source: reference (56).

## Processes Operated in Germany

There are five main steps to the Fischer-Tropsch (normal-pressure) process as practiced in Germany:

- I. Synthesis-gas manufacture.
- II. Gas purification.
  - A. Removal of water and dust.
  - B. Removal of hydrogen sulfide and organic sulfur compounds.
- III. Synthesis of hydrocarbons.
- IV. Condensation of liquid products and recovery of gasoline from product gas.
- V. Fractionation of synthetic products.

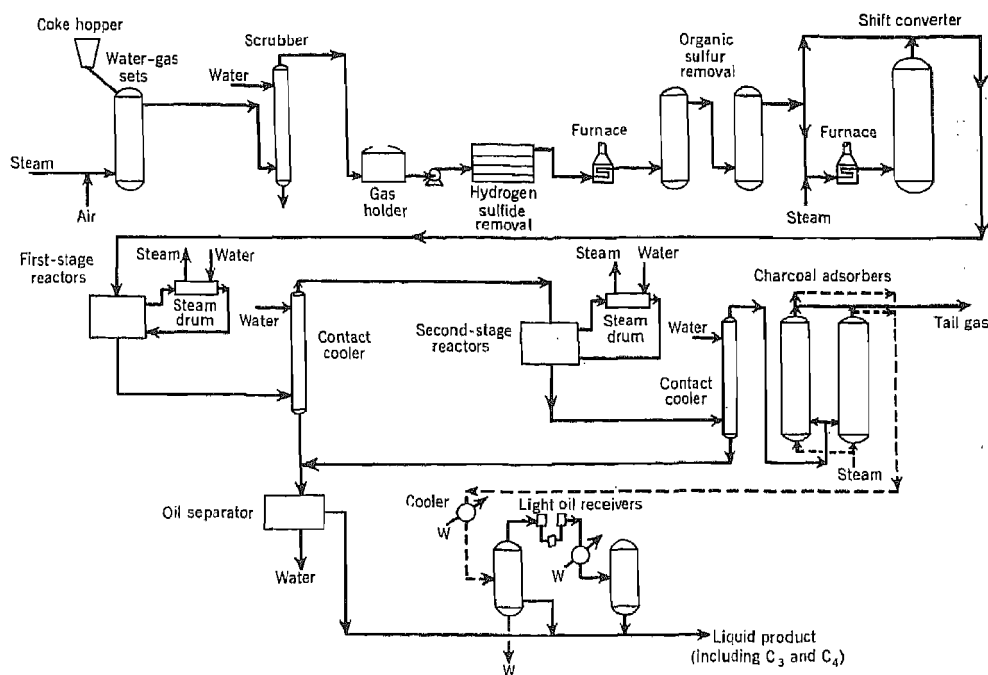


Fig. 3. Flow sheet of Fischer process at Oberhausen-Holtien.

Figure 3 gives a flow sheet of the process as carried out at Oberhausen-Holtien. However, the order of steps does not follow the above outline exactly.

**Generation of Synthesis Gas.** Synthesis gas was generated at the first commercial Fischer-Tropsch plant at Oberhausen-Holtien from water gas of the composition 51% hydrogen, 40% carbon monoxide, 5% carbon dioxide, and 3% nitrogen. Since the optimum gas composition for the Fischer synthesis was approximately two parts of hydrogen to one part of carbon monoxide, the water gas was enriched with hydrogen by the water-gas shift reaction, that is, by converting part of the carbon monoxide with steam to carbon dioxide and hydrogen. Approximately one-fourth of the water gas was passed over a catalyst bed at about 490°C., and the product was blended with

the remaining three-fourths of the water gas. The average analysis of the hydrogen-enriched gas was 55% hydrogen, 28% carbon monoxide, 14% carbon dioxide, and 3% nitrogen.

The desirability of producing large quantities of synthesis gas continuously from coal or lignite, rather than intermittently from coke, was evident from the beginning of the commercialization of the Fischer synthesis. By 1936, several such processes were developed and in operation. The Didierwerke generator is heated externally through the outside wall, and steam continuously passes through the interior. In the Koppers process, heat of gasification is supplied by superheated steam and recycle gas. The recycle gas and steam are superheated in regenerators which alternately superheat the gases for thirty minutes and are then heated in turn for thirty minutes by combustion of a portion of the product gas.

Operation of the Didierwerke and Koppers generators on peat gives product gases containing 50-55% hydrogen, 28-32% carbon monoxide, 7-12% carbon dioxide, and 2-10% nitrogen. When converted to a synthesis gas of two parts hydrogen to one part carbon monoxide, the gases would have essentially the same composition as the synthesis gas produced by enriching the gas from the water-gas sets at Oberhausen-Holten.

**Purification of Synthesis Gas (33a,73).** The raw synthesis gas after enrichment with hydrogen in the water-gas shift converters first flows to a water scrubber where carbon, tar, and water are removed and is then passed over thin beds of hydrated iron oxide (Luxmasse), to remove hydrogen sulfide. The gas then still contains 2-10 grains per 100 cu.ft. of organic sulfur, chiefly carbonyl sulfide and carbon disulfide, definitely more than the tolerance of 0.1 grain of sulfur per 100 cu.ft. It is passed over a mixture of hydrated iron oxide and sodium carbonate at 200-300°C. The organic sulfur is catalytically converted to hydrogen sulfide, which is then removed.

Carbon dioxide is not removed from the synthesis gas in the normal-pressure plants, since it has no significant effect on the results when using cobalt catalyst. In some medium-pressure plants, carbon dioxide is washed from the synthesis gas with water to reduce the volume of gas handled. If an iron catalyst is to be used in a plant, the removal of carbon dioxide is decidedly beneficial.

**Synthesis Reactors.** The reactor used for the low-pressure synthesis consists of a bundle of flat plates stacked horizontally with cooling tubes penetrating the bundle perpendicular to the plates. The plates are 0.063 in. thick and the distance between plates is 0.29 in. The cooling tubes are approximately 1 in. in diameter and are placed on 2.2-in. centers. The bundle is enclosed in a rectangular box. Water under pressure is used as the coolant. The cooling surface, plates and tubes, amounts to 115 sq.ft. per cubic foot of catalyst volume, and the weight of the assembly is 225 lb. per cubic foot. The height of the catalyst bed is 8 ft. A unit contains approximately 360 cu.ft. of catalyst and has an average capacity of about 35,000 cu.ft. of synthesis gas per hour or about 30 bbl. of liquid products per day.

The elaborate construction of the low-pressure reactor was necessary to assure removal of the heat of reaction from the catalyst bed, a problem made quite severe because of the tendency of the reaction to produce increased amounts of methane at too high temperatures. The thin, flat, plate construction was never meant to hold pressure, and so a new type of converter had to be developed for the medium-pressure synthesis. Double tubes were substituted for the flat plates, with the catalyst in the annulus between tubes and the coolant circulating outside the outer tube and inside

the inner tube. Water under pressure is used as coolant. The diameter of the outside tube is 1.9 in. and of the inside tube about 1 in. The width of the annulus is 0.4 in. The tubes are placed on 2.2-in. centers. A single converter contains 2,000 tubes, approximately 15 ft. in length. It has a cooling surface of 60 sq.ft. per cubic foot of catalyst volume and weighs 280 lb. per cubic foot. The catalyst volume is 360 cu.ft., and the capacity is the same as for the low-pressure unit, that is, about 30 bbl. of liquid product per day.

The double-tube unit was not as satisfactory as the flat-plate unit as a heat-transfer apparatus and, when tested at normal pressure, gave slightly lower yield of oil than the flat-plate unit.

#### **Condensation of Liquid Products and Recovery of Gasoline from Product Gas.**

At Oberhausen-Holten, the total effluent of the first-stage synthesis reactors is cooled in a tower countercurrent to cold water. The water product of the synthesis and the bulk of the liquid hydrocarbons are condensed and removed from the bottom of the tower mixed with the cooling water. The oil is separated from the water in a drum and the oil product flows to the fractionation system. The gas leaving the cooling tower flows to the second-stage synthesis reactors. The effluent from the second-stage reactors passes through a water cooling tower. The condensate from this cooler is added to the condensate of the first tower. The gas passes through charcoal adsorbers. The gasoline adsorbed by the charcoal adsorbers is displaced with steam and sent to storage.

**Production Data.** Table IV presents typical values of the composition of technical-scale reaction products of the normal- and medium-pressure syntheses.

**Preparation of Synthesis Catalyst.** Two catalysts were used commercially in Fischer plants. The first was the so-called standard cobalt catalyst, which had the composition 100 Co:18 ThO<sub>2</sub>:100 kieselguhr. The second was 100 Co:5 ThO<sub>2</sub>:7.5 MgO:200 kieselguhr. The substitution of magnesia for part of the thorium was made chiefly for economic reasons. Synthesis catalyst was first shipped after impregnation with paraffin oil, and later in drums blanketed with carbon dioxide gas.

A carefully measured solution of nitrates of cobalt and thorium (and magnesium, if used) is heated nearly to boiling and added to the correct amount of a boiling solution of sodium carbonate. After just sufficient stirring to assure mixing, kieselguhr is added, and the precipitate is immediately filtered and the filter cake washed with water. The entire mixing procedure generally involves less than two minutes. It is important to avoid too long a contact between the kieselguhr and sodium carbonate. The washed filter cake is extruded, dried, and screened. The sized catalyst is reduced with hydrogen in comparatively thin layers at 360–400°C. and atmospheric pressure.

Spent catalyst is reworked by first digesting it with nitric acid to extract the cobalt and thorium (and magnesium). The solution is freed of the kieselguhr residue by filtration, and sodium carbonate is added to precipitate nickel, iron, aluminum, and thorium. The thorium is then recovered from the precipitate and added back to the final solution. Calcium is removed by precipitation as the fluoride, and the solution is then ready for fortification with fresh nitrates of cobalt, thorium, and magnesium, as may be required.

**Decline in Catalyst Activity.** In normal-pressure synthesis (but not in medium-pressure synthesis), it is necessary to regenerate the catalyst every 1–2 months by treatment with hydrogen at synthesis temperature. After several months of synthesis, a decline in the catalyst activity is observed which cannot be restored by hydrogen treatment at synthesis temperature. A hydrogen treatment at a temperature higher than the normal operating temperature would be favorable, but there is no provision for heating the converters beyond the normal operating range. The spent cobalt catalyst is reworked as described above.

The rate of decline of the activity of the synthesis catalyst in the commercial converters is dependent upon the degree of gas purification (sulfur, dust, water, etc.) and also the care with which the synthesis is controlled (constancy of gas flow, gas composition, temperature, etc.). The importance of a close control of the process has been amply demonstrated by the different yields obtained with

TABLE IV. Normal- and Medium-Pressure Syntheses.

Constituent	Wt. % of total products listed <sup>a</sup>	d <sub>4</sub> <sup>b</sup>	Olefins, vol. %	B.p. index <sup>c</sup>	Mol. wt. (av.)	No. C atoms	Cloud pt., °C.	Pour pt., °C.	Octane No., research method	Cetane No.	
										Motor	Research
Normal-Pressure Synthesis <sup>e</sup>											
Gasol (C <sub>3</sub> + C <sub>4</sub> )	12	—	50	—	—	C <sub>3</sub> + C <sub>4</sub>	—	—	—	—	—
Gasoline, to 185°C.	49	0.689	37	108	100	C <sub>4</sub> -C <sub>10</sub>	—	—	52	—	—
Gasoline, to 200°C.	54	0.693	34	115	115	C <sub>4</sub> -C <sub>11</sub>	—	—	49	—	—
Diesel oil, 185-320°C.	29	0.760	15	245	190	C <sub>11</sub> -C <sub>18</sub>	-13	-18	—	87	100
Diesel oil, 200-320°C.	24	0.766	13	260	205	C <sub>12</sub> -C <sub>18</sub>	-5	-9	—	92	105
Soft paraffins, 320-450°C.	7	0.900	$\left\{ \begin{array}{l} \text{Iodine} \\ \text{value} \end{array} \right\}$	—	—	>C <sub>15</sub>	—	—	—	—	—
Hard paraffins, >450°C.	3	0.930	2	—	—	—	—	—	—	—	—
Medium-Pressure Synthesis <sup>d</sup>											
Gasol (C <sub>3</sub> + C <sub>4</sub> )	—	—	30	—	—	66% C <sub>4</sub> 33% C <sub>3</sub>	—	—	—	—	—
Gasoline, to 185°C.	35	0.685	20	110	100	C <sub>4</sub> -C <sub>10</sub>	—	—	28	—	—
Gasoline, to 200°C.	40	0.689	18	120	115	C <sub>4</sub> -C <sub>11</sub>	—	—	25	—	—
Diesel oil, 185-320°C.	35	0.760	10	240	190	C <sub>11</sub> -C <sub>18</sub>	-7	-11	—	87	100
Diesel oil, 200-330°C.	35	0.766	8	255	205	C <sub>12</sub> -C <sub>19</sub>	-2	-5	—	92	105
Soft paraffins >320°C.	30	0.90	$\left\{ \begin{array}{l} \text{Iodine} \\ \text{value} \end{array} \right\}$	—	—	>C <sub>18</sub>	—	80°	—	—	—
>330°C.	25	0.90	2	—	—	>C <sub>19</sub>	—	80°	—	—	—

<sup>a</sup> Total yield per cubic meter of synthesis gas: normal-pressure synthesis, 148 grams; medium-pressure synthesis, 145 grams of liquid products and 10 grams of gasol.

<sup>b</sup> The boiling point index is the sum of the temperatures at which 5, 15, 25 . . . 95 vol. % distill over, divided by 10.

<sup>c</sup> At 1 atm.; 180-95°C.; catalyst, 100 Co:5 ThO<sub>2</sub>:7.5 MgO:200 kieselguhr; 1 CO:2 H<sub>2</sub> (18-20% inert components); throughput, 1 cu.m. synthesis gas/(kg. Co)(hr.); two stage; no recycle.

<sup>d</sup> At 7 atm. abs.; 175-95°C.; catalyst, 100 Co:5 ThO<sub>2</sub>:7.5 MgO:200 kieselguhr; 1 CO:2 H<sub>2</sub> (18-20% inert components); throughput, 1 cu.m. synthesis gas/(kg. Co)(hr.); two stage; no recycle.

<sup>e</sup> Approximate.

Source: Piehler, H., "Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen," *Technical Oil Mission Rept.* (Library of Congress), Reel 259, Frames 467-654 (1947).

the same catalyst and the same converter in different plants. However, under the most favorable conditions, the activity declines at a rate which necessitates replacement of the catalyst about once a year.

In a spent catalyst, the material at the top of the converter contains a comparatively high amount of sulfur (up to about 0.8%), since the first part of the catalyst removes the last traces of sulfur of the gas during the synthesis. It also contains large amounts of combustible matter (carbon, resins, etc.), which cannot be removed by extraction or by hydrogen treatment at synthesis temperature. The formation of these materials is the result of the higher temperatures which prevail at the top of the reactor where the bulk of the reaction takes place. As the top catalyst becomes inactive, the zone of major reaction moves down the reactor until eventually the remaining catalyst is no longer adequate for the minimum operable conversion, and the catalyst must be replaced.

### Later Development in Germany

Some important development work was performed in Germany during World War II; some of this was never commercialized only because of the lack of opportunity. Although the results were not available to American workers until after the war, this work forms a part of the German contribution to the art of synthesis, and it is worthy of review.

**Schwarzheide Experiments.** In 1943, Germany was facing a possible shortage of cobalt and there was considerable anxiety as to whether the synthesis plants then operating could convert to iron catalysts without serious alterations. As a result, an intense campaign was initiated by the German government to develop an iron catalyst which would perform adequately in existing equipment. The best of the yields obtained were about 15% less than those realized with cobalt catalyst (103–125 grams of oil per cubic meter of synthesis gas). However, the feasibility of producing liquid hydrocarbons with iron catalysts in existing equipment was proved.

**Gas Recycle Operations.** Full-scale medium-pressure converters were operated on an experimental basis returning a part of the tail gas to the reactor (Lurgi, Ruhrchemie, Hoesch). The recycle amounted to 2–3 times the volume of fresh synthesis gas. Operating the reactors at the same fresh synthesis gas rate, and keeping other conditions the same as for the normal single-pass operation, the output of the converter was essentially unchanged but the product was more olefinic. With single-pass operation, the olefin content of the gasoline was 39% and of the Diesel oil, 23%, whereas with recycling (1:3) the corresponding olefin contents were 61 and 43%, respectively.

Similar recycle experiments with iron catalyst in pilot plants showed that operations at temperatures above the normal synthesis temperature, that is, 230°C. and 275°C. instead of 200°C., give more volatile and more olefinic products:

Temp., °C.	Paraffin fraction		Diesel oil fraction		Gasoline fraction	
	Total, %	Olefin content of fraction, %	Total, %	Olefin content of fraction, %	Total, %	Olefin content of fraction, %
230	60	—	20	45	20	60
275	8	—	21	60	71	75

The chief purpose of the recycle gas in the experiments described above was to alter the chemistry of the synthesis. Another type of recycle operation was tried, the chief purpose of which was to alter the heat-transfer mechanism. By circulating as much as 100 volumes of recycle per volume of fresh synthesis gas, it is possible to absorb



all of the heat of reaction as sensible heat of the products without the temperature of the gas increasing more than 10°C. Work on this high-recycle-rate process was done on a pilot-plant scale by Michael (46). Using ammonia synthesis catalyst at 325°C., a unit capacity of about 2.5 times that of the commercial converters was obtained. This was possible because heat transfer was not as critical as it was in the commercial converters. Over 80% of the product boiled in the gasoline range. At 195°C., the product resembled more closely the product of the commercial units, and the unit capacity was of the same order. This high recycle gas process was abandoned because of the uneconomic aspects of circulating such large volumes of gas.

**Synthesis with Catalysts Suspended in a Liquid Medium.** Much work was successfully performed with the catalyst suspended in liquid mediums instead of a fixed catalyst bed. The efficiency of the catalyst is determined essentially by the uniform dispersion of the catalyst and the synthesis gas through the medium. With the catalyst suspended in oil, results were obtained comparable with those for fixed-bed operations. In other experiments oil was circulated over a fixed-bed catalyst (52). In this scheme, the oil leaving the reactor is cooled and then returned to the reactor. A portion of the oil is continuously bled off for the recovery of synthesis products. At 25 atm., with a carbon monoxide-hydrogen ratio of 1:0.82 and two stages, 128 grams of liquid hydrocarbons was produced per cubic meter of synthesis gas, along with 22 grams of  $C_3 + C_4$ , and 20-30 grams of  $C_1$  and  $C_2$  hydrocarbons.

### Early Development Outside Germany

Interest in the Fischer-Tropsch process was exhibited outside Germany as early as the middle 1920's. Accounts of experimental work on hydrocarbon synthesis, carried out in England, were published in 1926-28 (13,14,17). In 1936, Myddleton and Walker published the results of their experiments (51), and in 1939, Craxford and Rideal published the first of their articles on the reaction mechanism (8,9). The British Fuel Research Board reported the erection of a 4-gal.-per-day pilot plant in 1937, and a year later Myddleton described a 150-gal.-per-day pilot plant erected to test the Robinson-Bindley modification of the Fischer-Tropsch synthesis (50). (The chief modification was the use of a gas having a lower ratio of hydrogen to carbon monoxide than the 2:1 ratio used by Fischer.)

In France in 1937, the Société Courrières-Kuhlmann completed the erection of a plant at Harnes in the Pas de Calais district. This plant was operated under license from Ruhrchemie. It produced slightly less than 1000 bbl. per day of liquid hydrocarbons. In the period 1929-38, there were reports of work done in Japan on cobalt catalysts for the normal-pressure synthesis (31,32,40,41). In 1938, two full-scale plants were operating in Japan under Ruhrchemie license, one at Fushan and the other at Omudu (Kyushu). The combined output of these plants was approximately 2500 bbl. per day. In 1943, a full-scale medium-pressure plant using iron catalyst was designed for Italy, but erection was only started by the end of World War II.

In the U.S., papers were published on the synthesis of higher hydrocarbons from water gas (64,65). Egloff reported work by Universal Oil Products in 1937 on cracking of the high-boiling fractions of Fischer liquid to obtain a gasoline of improved quality (15,16). In 1938, a group known as Hydrocarbon Synthesis, Inc., consisting of certain petroleum interests in the U.S. and I. G. Farben, entered into an agreement with Ruhrchemie, whereby, among other things, the group obtained the exclusive

right to license the Fischer synthesis outside Germany. The American interests included Standard Oil Development Company, Standard Oil Company (of Indiana), Shell Development Company, and The M. W. Kellogg Company. In accordance with this agreement, the interested parties carried on research and development work during the period 1938-40. There is little account of this work in the literature, but it is believed to have progressed only to the stage of confirmatory experiments and pilot-plant operations on the synthesis reaction based on the work of Fischer and his co-workers. Some work was done on studies of ancillary processes for the conversion of natural gas to water gas and the upgrading of the Fischer liquid to fuels comparable in quality to fuels then being produced from natural petroleum.

With the event of World War II, Hydrocarbon Synthesis, Inc., was dissolved and cooperation between Germany and the U.S. ended.

### Development in the U.S.

Postwar activity has centered in the U.S. Toward the end of World War II, when the consumption of crude in the U.S. was at an all time high, interest in the Fischer-type synthesis was revived. In the intervening years, development work has been carried on by a large number of organizations. This work has had two general aims. One of immediate interest was to develop an economic process for the conversion of natural gas or refinery fuel gases to synthetic gasoline. The second, a part of the petroleum industry's long-range planning, was the conversion of other carbonaceous materials such as coal, lignite, and heavy pitches to liquid fuels.

The amount of money spent to date on this development work in the U.S. is estimated to be well in excess of \$10,000,000, exclusive of the capital required to build the first commercial plant. Not all of the results have been published to date, but news reports indicate that among those doing work are: The Texas Company, Standard Oil Development Company, Shell Development Company, Standard Oil Company (of Indiana), Stanolind Oil and Gas Company, Pittsburgh Consolidation Coal Company, The M. W. Kellogg Company, Cities Service Oil Company, Gulf Oil Corporation, Phillips Petroleum Company, Socony-Vacuum Oil Company, Inc., Blaw-Knox Company, Koppers Company, Inc., U.S. Bureau of Mines, and Hydrocarbon Research, Inc. Publications cover the production of synthesis gas (68), mechanism of synthesis (36,37,42,62,70), and commercial aspects of the synthesis (34,39,48,59,61,67).

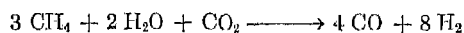
### PRODUCTION OF SYNTHESIS GAS IN THE U.S.

In the U.S., it is generally more economical to make synthesis gas from natural gas than from solid fuels. Methane and its homologs can be converted into suitable carbon monoxide mixtures using two basically different methods. In the first, methane can be converted to carbon monoxide and hydrogen by partial combustion with oxygen:



No catalyst is required for this reaction, which is carried out at 2500-2800°F. and 200-300 p.s.i. (39).

In the second method, methane is converted into synthesis gas with steam and carbon dioxide:



This reaction must be carried out in the presence of a catalyst (usually consisting largely of nickel) at 1600–1700°F. and atmospheric pressure. The conversion requires additional heat and can be carried out in high-temperature-alloy tubes fired in a furnace (27,58).

Much development work has been carried out in the U.S. on the production of synthesis gas from coal, which may be of interest in the future, if coal replaces natural gas as a raw material. The Bureau of Mines has tested suitable gasification processes in several pilot plants, and in a demonstration plant at Louisiana, Mo. This plant uses the Koppers-type dust gasification system, based on continuous gasification of suspended powdered coal with oxygen and superheated steam (5).

#### HYDROCOL PROCESS

The only process which is currently being reduced to practice in the U.S. and the only American development with which the authors have been associated is the Hydrocol process.

The Hydrocol process was developed by Hydrocarbon Research, Inc., under the sponsorship of The Texas Company, Standard Oil Development Company, Socony-Vacuum Oil Company, La Gloria Corporation, J. S. Abererombie Company, and Hydrocarbon Research, Inc. Experimental work, including pilot-plant operations of all the major steps of the process, was carried out at Hydrocarbon Research's laboratories at Olean, N.Y., and Trenton, N.J. The first commercial Hydrocol plant was erected for Carthage Hydrocol, Inc., at Brownsville, Texas. It was designed by Hydrocarbon Research, Inc., and was erected by Arthur G. McKee & Company. Important contributions to the research, upon which the design was based, were made by The Texas Company, Stanolind Oil and Gas Company, and the Standard Oil Development Company.

In 1943, when P. C. Keith and his staff at Hydrocarbon Research, Inc., first studied the economics of synthetic fuels by the Fischer type of synthesis, it was obvious that the process as practiced commercially in Germany was not and would not be economical in the foreseeable future. The product could be marketed in the U.S. in quantity only as synthetic crude oil, and for a crude oil its cost was far too high. As an added burden, the synthetic crude oil differed significantly from any refined by the petroleum industry, and so the quality of the refined products and their cost were uncertain. A second fact was equally obvious: if a new process could be developed which would produce directly refined products, that is, a high yield of high-octane gasoline and a salable gas oil, and if the cost of producing the refined products could be markedly reduced from the cost of the Fischer products, then the new process might be very attractive for the conversion of natural gas to synthetic fuels. The new process would obviously require improvements both in the chemistry of the synthesis and in the engineering.

The basic chemistry of the synthesis with iron catalysts had already been well established (52,53,54). The desired improvements in the chemistry of the synthesis were three: the development of a cheaper iron catalyst; the operation of the synthesis at higher temperatures than had been found operable in the fixed-bed reactors of the Germans, in order that the large quantity of heat evolved during the synthesis could be recovered as useful energy; and the attainment of essentially the same yield of liquid per unit volume of gas with a feed gas having two volumes of hydrogen per

volume of carbon monoxide as was obtained by the Germans using an equimolal mixture, since the gas prepared from natural gas would have the former composition.

The major engineering problem was to increase the capacity of the reactor. In addition, simplification of the equipment was required. The capital cost of the Ruhr-chemie plant, even assuming it could produce refined products, was far too high. A multiplicity of small complicated units was used to generate the synthesis gas, to purify it, and to carry out the synthesis. Also the conservation and utilization of energy left much to be desired. What was needed was the radical, typically American, approach to engineering problems. Build a big plant and carry out various operations in single units or at most two or three units in parallel. Carry the conservation of material and energy to their economic optimum. Make the operation wholly continuous and dependable to the degree that plant shutdowns are dictated by normal maintenance and safety inspection requirements rather than by process requirements.

**Process Steps.** The basic steps of the first Hydrocol plant for conversion of natural gas to gasoline have been described by Keith as follows (39): (1) The recovery of about 0.25 gal. of natural gasoline and butane per 1000 cu.ft. of natural gas. At low concentrations, recovery of this natural product becomes economical only as an incremental operation of the Hydrocol process. (2) The separation of 40,000,000 cu.ft. per day of high purity oxygen from air (see *Oxygen*). (3) The partial combustion

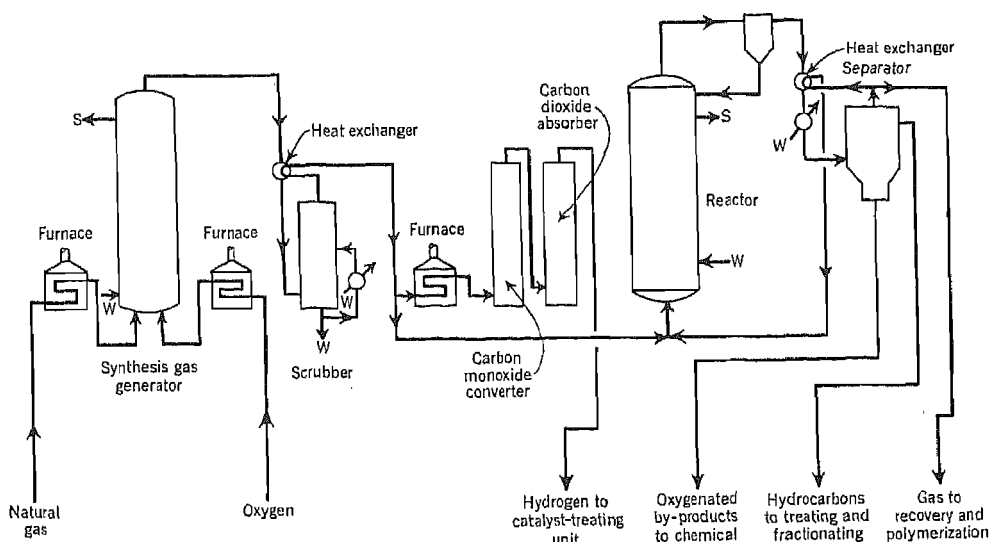


Fig. 4. Flow sheet of Hydrocol process.

of 64,000,000 cu.ft. per day of natural gas with the high-purity oxygen to produce a mixture of carbon monoxide and hydrogen. (4) The conversion of this mixture of carbon monoxide and hydrogen into gasoline and other synthetic products. (5) The separation of the gasoline and other synthetic products by fractionation and absorption techniques. (6) The treatment of the gasoline to remove oxygenated compounds, polymerization of the propylene and butylene, rerunning, blending, etc. (7) The manufacture and revivification of catalysts.

A flow diagram of the gas-generation and synthesis sections is shown in Figure 4.

Details of the design of the full-scale plant have not been disclosed, but Latta and Walker have described a similar plant, to handle "Hugoton gas" (nitrogen-rich natural gas), designed by Hydrocarbon Research, Inc. with the collaboration of the research and engineering staff of Stanolind Oil and Gas Company (45). With a nominal rating of 6,400 barrels per day of synthetic liquid hydrocarbons, this plant requires the following: (1) An oxygen plant having a capacity of approximately 2,000 tons of oxygen per day. This plant was designed in two units, whereas it would have required 12-15 of the largest units ever built in Germany. (2) A gas-generation plant having a capacity of approximately 250,000,000 standard cubic feet of synthesis gas per day. This plant was designed in two units. (The Brownsville plant has only a single unit.) It would have taken about 6 of the largest Didierwerke or Koppers units ever built to produce an equivalent quantity of synthesis gas. (3) A synthesis section having a capacity for combined feed gas of nearly 1,000,000,000 standard cubic feet per day. This section was designed with two units. Nearly 100 of the largest German reactors would be required for the same job. (4) A single fluid-bed treating unit, and more or less conventional recovery and catalytic polymerization units.

**Equipment.** The cylindrical converter contains a number of cooling tubes in which water at elevated pressure is used to remove the exothermic reaction heat. The fluidized catalyst is in constant movement around the vertical water tubes, thereby enhancing the heat transfer. Synthesis gas flows from the bottom of the converter to the top with a velocity which keeps the catalyst suspended. Some of the catalyst is entrained by the effluent and is subsequently separated and returned to the reactor.

The method of preparation of the catalyst is quite simple, and inexpensive raw materials such as iron ore can be used. Hence reworking is unnecessary, yet it gives yields per cubic meter of synthesis gas that are as high as the best yields obtained with cobalt catalysts, and this in spite of vastly greater gas throughput per unit of catalyst. In contrast to working with fixed-bed catalysts, with fluidized catalysts the production of large amounts of solid paraffin must be avoided, since the products must leave the reactor as vapor or remain in the catalyst, and large catalyst deposits affect fluidization.

TABLE V. Comparison between Fixed-Bed and Fluidized Catalysts.

Operating data	German fixed-bed catalyst	Hydrocol fluidized catalyst
Temperature, °C.....	180-220	300-350
Throughput, vol. gas/(vol. catalyst)(hr.) <sup>a</sup> .....	100	3,000
Heat of reaction, kg.-cal./(cu.m. catalyst)(hr.).....	50,000	1,500,000
Yield of C <sub>3</sub> and higher, grams/cu.m. synthesis gas.....	165	165
Yield of C <sub>3</sub> and higher, kg./(cu.m. catalyst)(hr.).....	16.5	495
Synthesis converters required for production of 1,000,000 tons/yr...	700-1,000	5

<sup>a</sup> In the case of the fluidized catalyst, the expanded volume of the catalyst is considered.  
Source: reference (52b).

The deposition of carbon is always a major problem in the performance of the synthesis with fixed-bed iron catalysts. It is necessary to prevent this carbon formation almost completely. This is accomplished by working with the lowest possible temperatures, hydrogen-rich synthesis gases, and catalysts of certain composition and method of manufacture. The production of small amounts of carbon is not so serious when working with fluidized catalysts. Larger amounts of carbon, however, are unde-

sirable because the carbon results in damage to the physical structure of the catalyst and in a decrease in the catalyst density.

Table V compares the synthesis conditions for the German process with one set of data from a Hydrocol pilot plant.

**Products.** The product of the Hydrocol synthesis is predominantly high-octane gasoline (85-90% of the liquid product). It has an octane number after isomerization of about 80 motor method and 90 research method, making it equal to the best gasoline currently produced in quantity by cracking of natural petroleum. The light gas oil obtained (15% or less), after mild treatment, is suitable for Diesel fuel or can be readily converted to high-octane gasoline. It also is ideal for synthesis of certain chemicals, because of its high concentration of straight-chain monoolefins. The Hydrocol plant also produces a very minor amount of heavy fuel oil.

TABLE VI. Typical Yields of Oxygenated Products for a Plant Producing 1000 Barrels of Hydrocarbons per Day.<sup>a</sup>

Oxygenated product	Amount, 1000 lb./yr.
<i>Water-dissolved chemicals</i>	
Alcohols:	
Methanol.....	60
Ethyl.....	8,030
Isopropyl.....	164
<i>n</i> -Propyl.....	1,890
Butyl.....	871
Amyl and higher.....	270
<i>Total alcohols.....</i>	<i>11,285</i>
Aldehydes:	
Acetaldehyde.....	1,310
Propionaldehyde.....	488
Butyraldehyde.....	457
<i>Total aldehydes.....</i>	<i>2,255</i>
Ketones:	
Acetone.....	1,630
Methyl ethyl ketone.....	471
Methyl propyl ketone.....	194
Methyl butyl ketone.....	53
<i>Total ketones.....</i>	<i>2,348</i>
Acids:	
Acetic.....	3,930
Propionic.....	1,030
Butyric.....	733
Valeric and higher.....	168
<i>Total acids.....</i>	<i>5,861</i>
<i>Total water-dissolved chemicals.....</i>	<i>21,749</i>
<i>Oil-dissolved chemicals</i>	
Alcohols.....	2,710
Aldehydes and ketones.....	2,780
Acids.....	2,740
<i>Total oil-dissolved chemicals.....</i>	<i>8,230</i>

<sup>a</sup> The oxygenated products average between 10 and 20% of the total product.

The characteristics of the Hydrocol gasoline have been described by Bruner (7). The sample described was obtained by blending treated (isomerized) gasoline fraction in the ratio of production with polymerized  $C_3 + C_4$  fraction, and it was brought up to a 9.2-pound Reid vapor pressure with *n*-butane. The octane rating clear is 80.2 motor method, and 91.4 research method. After the addition of 3 ml. of tetraethyl lead per gallon, the octane ratings are 84.1 and 97.2, respectively. It has an A.P.I. gravity of 65.8. An A.S.T.M. distillation yielded the following results:

Amt. distilled, % . . . . .	Initial	10	50	90	End point
B.p., °F. . . . .	99	133	222	342	394

The composition of the chemicals dissolved in the water product has been reported as shown in Table VI (12,66). Alcohols are the largest single class followed in order by acids, ketones, and aldehydes. The two-carbon compounds predominate, followed by those having increasingly greater number of carbon atoms.

#### SYNTHESIS WITH OIL CIRCULATION

The Bureau of Mines has carried out tests at Brucetone, Penna., on two other types of processes (10): one uses fixed or slightly moving beds of granular catalysts

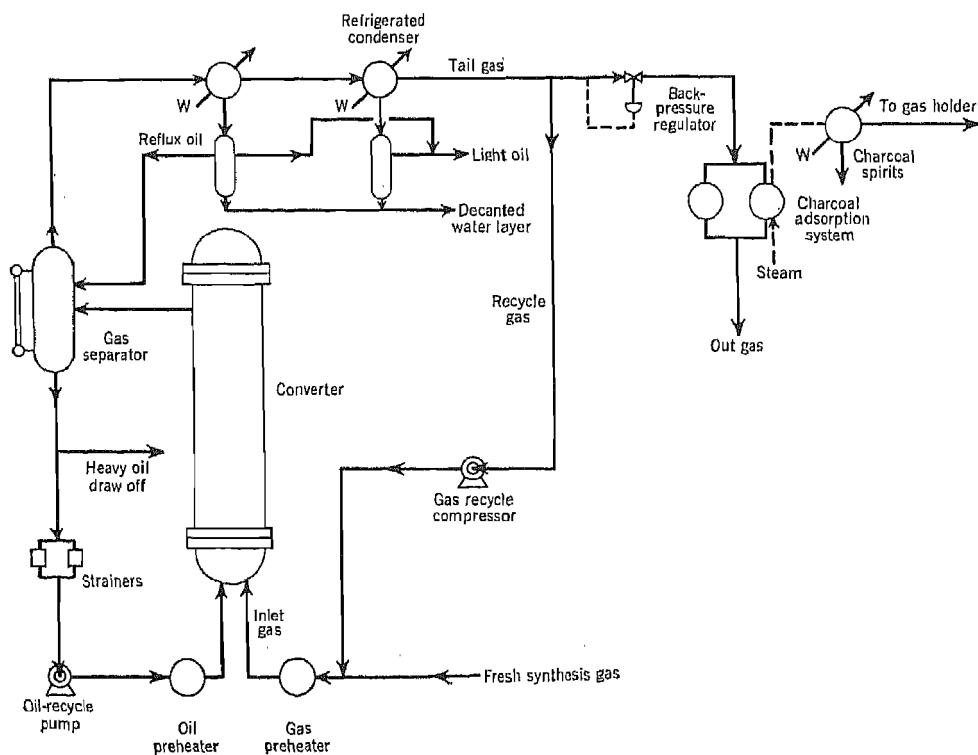


Fig. 5. Bureau of Mines Fischer-Tropsch oil-circulation process (10).

with internal cooling by direct heat exchange with recycling oil; the other uses suspensions of finely powdered catalysts in oil (oil-slurry system). The first process will be used for the demonstration plant in Louisiana, Mo. Synthesis experiments with direct

heat exchange by oil recycle have also been carried out by I. G. Farben, and by the Standard Oil Development Company and The Texas Company.

Figure 5 shows a flow diagram of the Bureau of Mines pilot plant for synthesis with oil circulation. The reactor consists of a cylindrical vessel into which the synthesis gas and recycle oil enter at the bottom. The catalyst is either in a fixed bed, or else it is kept in slight motion by sufficiently increasing the gas velocity. The increase in the bed height amounts to 25–35%. In the pilot plant, the gas and oil are heated before entering the converter, but, in a full-scale plant, cooling of the recycle oil would be required. The products of the reaction pass to a gas separator, which acts as a sump for recycle oil, and from which the excess is drawn off as a heavy oil product. The gas then passes to a water condenser and a refrigerated condenser, which yield a light oil (which can, if required, be added to the recycle) and a water layer containing the oxygenated by-products, mostly ethyl alcohol. The remaining gas passes through

TABLE VII. Operating Conditions with Oil-Submerged Fixed- and Moving-Bed Catalysts.<sup>a</sup>

Operating conditions	Catalyst bed	
	Fixed, 8-ft. height, 4–6 mesh	Moving, 4-ft. static height, 5.2-ft. expanded, 8–16 mesh
Weight of iron charged, lb. ....	42.8	24.7
Ratio of H <sub>2</sub> -CO in feed gas ....	1:1	1.3:1
Total catalyst age, hr. ....	2300	2670
Temperature (max.), °C. ....	260	245
Temperature differential, °C. ....	16	6
Pressure drop, p.s.i.		
Start of experiment. ....	4	5
End of experiment. ....	49	5
Feed-gas rate, cu.ft./hr. ....	124	123.2
Space velocity, vol./(vol.)(hr.)		
Based on settled catalyst. ....	300	601
Based on expanded catalyst. ....	—	462
Space-weight velocity, cu.ft. feed gas/(lb. Fe)(hr.) ....	2.88	4.97
Recycle ratio (tail gas:fresh gas) ....	2.0:1	1.0:1
Conversions:		
CO, % ....	69.9	79.8
H <sub>2</sub> , % ....	69.9	63.0
H <sub>2</sub> + CO, % ....	69.9	70.3
Usage ratio (H <sub>2</sub> :CO) ....	1.0	1.04
Cu.ft. H <sub>2</sub> + CO (lb. Fe)(hr.) ....	2.01	3.49
C <sub>1</sub> + C <sub>2</sub> , grams/cu.m. of feed gas ....	24.5	21.9

<sup>a</sup> At 300 p.s.i.g.

Source: reference (10).

TABLE VIII. Liquid Product Distribution (Pilot Plant).<sup>a</sup>

Product	Yield, wt. %	
	1.3 H <sub>2</sub> :1 CO	1 H <sub>2</sub> :1 CO
Gasoline (C <sub>3</sub> +–400°F.) ....	54.2	52.4
Diesel oil (400–600°F.) ....	10.4	10.0
Heavy distillate (600–842°F.) ....	12.2	16.0
Wax (>842°F.) ....	11.5	11.1
Oxygenated compounds ....	11.7	10.5

<sup>a</sup> Space velocity, 600 vol./(vol.)(hr.).

Source: reference (10).



charcoal adsorbers leaving a tail gas. On regenerating the charcoal with steam, a further liquid product, "charcoal spirits," can be obtained by refrigeration.

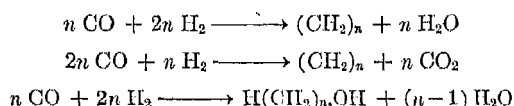
Table VII is a comparison of conditions in the oil-submerged fixed- and moving-bed catalyst operations. Table VIII shows typical products obtainable after refining. In order to obtain satisfactory synthesis gas conversion, it is necessary to carry out the reaction in two stages, preferably with intermediate removal of carbon dioxide.

### Mechanism of the Reaction

Much experimental work and thought has been devoted to the reaction mechanism for the catalytic reduction of carbon monoxide with hydrogen, but as yet no wholly satisfactory mechanism has been described.

The product of the catalytic reduction of carbon monoxide is a complex mixture of hydrocarbons, with or without alcohols, aldehydes, ketones, and fatty acids. The two exceptions to this are the syntheses of methane and of methanol, for these can be formed without significant quantities of by-products. However, when the linkage of carbon atoms is allowed to occur, the product contains a typically random distribution of a large number of different-size molecules. By varying catalyst and/or operating conditions, it is possible to control the average size and, to a degree, the type of molecule, but no fraction of the product is restricted to a single compound or even to a few compounds.

Complicated as the product of the Fischer-type synthesis is, it is still possible to illustrate its formation by three overall equations. These equations do not indicate in any way the reaction mechanism, but simply represent the stoichiometric relationship between reactants and products:



The four products are shown as water, carbon dioxide, hydrocarbons, and alcohol. Equations can also be written showing the formation of hydrocarbons of other types, or of aldehydes, ketones, and fatty acids. Although the above equations give no clue as to the reaction mechanism, they indicate certain basic actions, which must occur either directly or through intermediates. These are the rupture of the carbon-oxygen bond of at least some of the carbon monoxide present, and the forming of carbon-hydrogen and carbon-carbon linkages. Accompanying these more basic actions are secondary molecular rearrangements typified by dehydration, polymerization, alkylation, isomerization, cyclization, and probably, in some instances, even rupture of carbon-carbon bonds of large molecules.

The relative extent to which the several actions enumerated above proceed can be controlled, within limits, by proper selection of catalyst and operating conditions. To cite a simple example, the extent of carbon-to-carbon linkage is generally increased by decreasing temperature or by increasing the concentration of alkali on an iron catalyst. By making a number of changes, truly remarkable differences can be achieved. Indeed, this is the basis for the seven different syntheses founded upon the catalytic reduction of carbon monoxide (see Fig. 6).

**Products of the Different Syntheses.** Certain generalizations are evident from Figure 6. At intermediate temperatures, 250–350°C., and normal pressure, bulk

nickel and cobalt catalysts produce methane as the chief product. This was the synthesis of Sabatier. Ruthenium can also be used. When an active form of iron, or cobalt or nickel deposited on kieselguhr, is used at low temperatures, 150–250°C., the synthesis of higher hydrocarbons predominates. These hydrocarbons are almost wholly aliphatic and mostly saturated. This is the original Fischer-Tropsch synthesis. By increasing the pressure to 5–25 atm. and using cobalt on kieselguhr, higher hydrocarbons, including solid paraffins are obtained; when iron is used at a somewhat higher temperature, olefins and paraffins are obtained, together with significant amounts of alcohols and other oxygenated compounds (particularly at the higher pressures and intermediate temperatures, as shown in Figure 6).

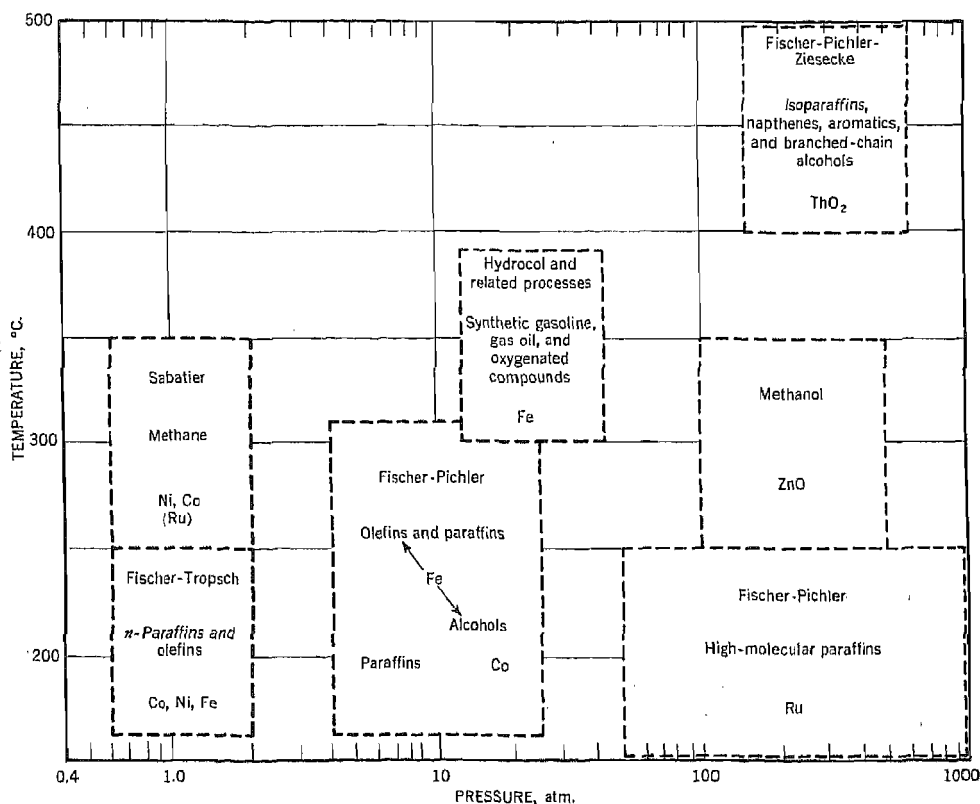


Fig. 6. Pressure-temperature ranges for different syntheses.

By increasing the temperature further to 300–75°C. and the pressure to 15–40 atm., the iron catalyst of the Hydrocol synthesis can be made to yield a liquid hydrocarbon fraction, which is chiefly olefinic and which boils predominantly in the gasoline range. This synthesis also yields a significant fraction of alcohols, etc.

By increasing the pressure to 100–1000 atm. and lowering the temperature to 150–250°C. and using ruthenium as the catalyst, very high-molecular compounds are formed (paraffin wax synthesis of Fischer and Pichler). At the same pressure but at somewhat higher temperature and with an oxide catalyst (for example, zinc oxide), methanol is the sole product (I.G. methanol synthesis). At still higher temperatures with thorium oxide as the catalyst, isoparaffins are formed (Fischer-Pichler-Ziessacke,

synthesis). Under certain conditions, small amounts of branched-chain chemicals such as isobutyl alcohol may be formed.

**Conversion of Metals to Carbonyls.** Nickel, cobalt, iron, and ruthenium form volatile carbonyls, and their formation is favored at temperatures around 200°C. In this temperature range, the balance between the rate of formation of carbonyls (which increases with temperature) and the equilibrium concentration of carbonyls (which decreases with temperature) is optimum for carbonyl formation. As the pressure is increased above atmospheric, a region is reached first for nickel, then cobalt, iron, and finally ruthenium, in which volatile carbonyls are formed in appreciable quantities. The use of nickel at low temperatures and at pressures above atmospheric is precluded, owing to the loss of nickel through the formation of carbonyl. Cobalt can be used up to 20–30 atm., iron possibly as high as 100 atm., and ruthenium above 100 atm.

Conditions which have proved optimum for the various hydrocarbon syntheses with nickel, cobalt, iron, and ruthenium catalysts are close to those necessary for appreciable carbonyl formation (the operation with ruthenium catalyst is actually in the range where carbonyl would form in appreciable quantities in the absence of hydrogen). However, both the carbonyl and reduction reactions are dependent upon the adsorption of carbon monoxide on the surface, and so it is not surprising that conditions beneficial to one are beneficial to the other.

Operation of the catalysts under conditions of appreciable volatile carbonyl formation leads to a rapid deactivation of the catalyst, long before the bulk of the metal is entirely converted to carbonyl. The probable explanation for this is that the active centers of these catalysts are the first to be converted to inactive carbonyl.

**Carbides as Intermediates of the Reaction.** Nickel, cobalt, and iron form carbides which are stable under synthesis conditions and which are present under synthesis conditions. Many theoretical and experimental attempts have been made to assign the role of intermediate to these carbides but not with complete success.

Early in the development, Fischer and his co-workers prepared carbides of iron and cobalt and treated them with molecular hydrogen. Under conditions that normally would have led to higher hydrocarbons, the result was not higher hydrocarbons but methane. However there is real doubt whether hydrogen alone would have the same effect as hydrogen under the conditions of the synthesis. Throwing further doubt on the significance of the foregoing experiment was the fact that Fischer was able to show that with at least one form of hydrogen higher hydrocarbons are formed: when the carbided catalysts were treated with dilute acids, the products were higher hydrocarbons.

More recently, Kummer, Dewitt, and Emmett carbonized iron and cobalt catalysts partly with normal carbon monoxide and partly with radioactive carbon monoxide ( $C^{14}O$ ) (43). The synthesis was then carried out with normal carbon monoxide and hydrogen. Only a small part of the initial products contained radioactive carbon, and radioactive particles continued to appear in the products over an extended period, whereas conceivably all of it would have appeared in the initial product and none in the subsequent product if carbide were an intermediate. However, there is a possibility that only a small amount of the radioactive carbide was contained in the active centers of the catalyst and that the radioactive carbon was being replaced continually by exchange reactions or otherwise from the inactive bulk of the catalyst to the active centers.

Other experimental observations which tend to contradict the carbide theory but which still are not definitive are the syntheses of higher hydrocarbons at high pressure over ruthenium and over thorium oxide catalysts, both in the absence of carbides.

**Identification of Carbides by Thermomagnetic Measurements.** Whereas the role of the carbide as an intermediate is questionable, it appears probable that carbides are an essential part of the crystal lattice of some catalysts, particularly the iron catalyst. Considerable work has been done on the identification of carbides (4,19,33,55).

**Thermomagnetic Studies on Iron Catalysts.** The ferromagnetic properties of iron, iron carbide, and magnetite offered an approach to the problem of their identification. The spacing of their magnetic transition points (Curie points) is sufficient to make identification easy by thermomagnetic studies.

A type of magnetic balance developed by Lange and Mathieu (44) was used by Pichler and Merkel (55) for thermomagnetic measurements of catalysts at operating temperatures. Their results gave evidence of a carbide,  $\text{Fe}_3\text{C}$ , which exists in two forms, with Curie points 265 and 380°C. X-ray diffraction studies seem to confirm the existence of these two forms of  $\text{Fe}_3\text{C}$  (3,6,35,37).

**Kinetic Studies of the Synthesis (Determination of Activation Energy).** Eddus compared the velocity of synthesis and carbide formation on cobalt, nickel, and iron catalyst (11). The rate of the synthesis was in all cases many times greater than the rate of carbiding. The ratio of the rate of synthesis to the rate of carbiding increased with the duration of the experiment; in the case of cobalt and nickel, from 5 to 20-30, and in the case of iron from 2 to 8.

Weller observed during the very first moments of the carbon monoxide treatment of a cobalt-thoria-kieselguhr catalyst a very high carbon monoxide consumption, which diminished rapidly to a fairly steady, but much lower rate (70). Evidently a flash carbiding of the surface metal occurred, followed by a slower reaction of the bulk metal. The speed of the slower portion of the reaction is comparable to the speed of the synthesis reaction, as indicated by Weller's measurement of activation energies of 31 and 26 kg.-cal./mole, respectively. Weller also showed that the hydrogenation of a carburized cobalt catalyst with pure hydrogen is much faster than either the carbiding or synthesis reactions. This is quite different from the behavior of the iron carbides, which are stable with hydrogen under these conditions. Anderson, Krieg, Seligman, and O'Neill reported similar activation energies of 24-27 kg.-cal./mole for the synthesis (1).

**Thermodynamic Studies.** The question whether thermodynamic studies can be used for the explanation of the reaction mechanism of the Fischer-Tropsch synthesis has often been discussed (30,49,57,62,63,69). The composition of the reaction products of the synthesis does not correspond to a chemical equilibrium. The kind of hydrocarbons and oxygenated compounds produced is a result of the specific action of the catalyst, which, depending on the composition, favors one or the other conversion. Montgomery and Weinberger report that the distribution of paraffins obtained with the normal-pressure synthesis on cobalt is similar to that predicted by thermodynamic equilibrium calculations (47). But the type of hydrocarbon, with respect to branching and the position of the double bond in the olefins, cannot be explained by the laws of thermodynamics.

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**FULLER'S EARTH.** See *Clays (fuller's earth)*.

**FULMINATES; FULMINIC ACID, HONC.** See *Cyanides*, Vol. 4, p. 681; *Explosives (high)*, Vol. 6, p. 10.

**FUMARIC ACID, HOOCCH:CHCOOH.** See *Fermentation*; *Maleic acid*.

**FUMES.** See *Smokes and fumes*.

**FUMIGACIN, C<sub>32</sub>H<sub>44</sub>O<sub>8</sub>; FUMIGATIN, C<sub>8</sub>H<sub>8</sub>O<sub>4</sub>.** See *Antibiotics*, Vol. 2, pp. 22, 29, 34.

**FUMIGANTS; FUMIGATION.** See *Antiseptics*, Vol. 2, p. 80; *Insecticides*; *Sterilization, disinfection, fumigation*.

**FUNGI.** See *Fungicides*; *Microorganisms*.

## FUNGICIDES

The word "fungicide" comes from the Latin *fungus*, and the Latin *caedo*, to kill, hence, a fungus killer. In practice the term has come to denote a wider concept. A fungicide is a chemical that will kill, inhibit, or inactivate a fungus so that it does not grow. Some modern investigators are tending to substitute "fungitoxic" or "antifungal" for "fungicidal." See also *Antiseptics*; *Sterilization*. In general, the term carries a practical connotation, that is, a chemical that prevents fungi or molds from ravaging cloth, wood, plants, animals, and humans, or whatever else they attack. The word *prevents* is significant in this definition. With very few exceptions, present-day fungicides are protective. A piece of wood or an apple, once rotted, is beyond recovery, whatever the fungicide used. The fungicide must be applied before the infection has occurred or certainly before it has progressed very far. An antifungal compound must be very stable and resist action by heat, sunlight, rain, and oxidation, particularly since fungi are favored by high humidity. The compound must also have an affinity for the substance treated so that it will cling readily to it, but at the same time it must have at least some degree of solubility, in order to be able to exert a toxic action on the fungus.

Two general theories of fungicidal action have been advanced, the oligodynamic theory, and the suicide theory. The oligodynamic theory (action by a few) postulates that the insoluble residue of fungicides slowly liberates a few molecules into the water where the fungus is growing. These few molecules pass into the fungus along with its foodstuffs. Eventually enough accumulates to poison the fungus. Some experimental evidence exists to support the theory. The suicide theory, on the other hand, postulates that the fungus plays an active role. When a fungus grows, it excretes various substances into the medium, and it is postulated that these excretory products dissolve the fungicidal compound or convert it to a soluble compound that is toxic. According to this theory, the fungus, in effect, makes its own poison.

## AGRICULTURAL FUNGICIDES

Agricultural fungicides, together with insecticides, are the basis of an extensive manufacturing and distributing industry. Some crops like potatoes, apples, and citrus would disappear from the market without fungicides. For want of a satisfactory fungicide, Irish farmers harvested practically no potatoes for three straight years in the middle of the last century, and the resulting famine started large-scale migration from Ireland to the U.S.

Consumption figures for agricultural fungicides are difficult to come by. The U.S. Department of Commerce estimated the consumption of sulfur as a fungicide in 1947 as 79,000 tons. They estimated also that the use of dithiocarbamic acid derivatives climbed from 2,000 tons in 1947 to 4,000 tons in 1948. Groggins of the War Food Administration estimated that 50,000 tons of copper calculated as copper sulfate pentahydrate were needed in agriculture in 1945. McCallan of the Boyce Thompson Institute has estimated the annual consumption of formaldehyde and organic mercurials as 1,000 tons each.

In modern agriculture, fungicides are applied not only to foliage to control diseases like the potato blight, but also to seeds, to soil, and to fruits themselves. Fungicides are generally applied in water suspension with hydraulic sprayers. Sometimes they are applied as dusts, with extenders such as clay or talc. Dusting is more rapid,

but generally less effective than spraying. Ninety-nine per cent or more of the fungicides used are applied to the surface of plant parts to prevent the entry of parasites. In fact, the concept has so dominated the thinking, that the alternative, internal application, has all but been ignored. Internal treatment offers real promise as Stoddard and Dimond have shown (11). The types of compound used will probably be different, however. Water solubility will be a desirable rather than an undesirable property. See also *Insecticides*; *Sprays*.

The first agricultural fungicides used were elemental sulfur and compounds of heavy metals such as mercury and copper. They dominated the field until the 1930's, when adequate laboratory screening techniques were devised. During the 1940's, the flow of new compounds increased to a torrent, and it will probably increase further. Primary screening by modern technique involves a system, comprising fungus and chemical, in which spores and test compound are brought together in distilled water. By varying the dose of compound and reading the response in percentage of spores inhibited, one can generate a dosage-response curve. This curve can be reduced to a straight line by proper transformations (5). This line has two properties—position and slope. Position measures potency; slope indicates mechanism. Position can be used to measure the importance of particle size, of formulation, and of subtractive interference by other ingredients. Slope shows whether two compounds kill by the same or by a different mechanism. For example, the slope of the dosage-response curve of *o*-aminodiphenyl,  $C_6H_5C_6H_4NH_2$ , is steeper than that of *o*-hydroxydiphenyl (*o*-phenylphenol),  $C_6H_5C_6H_4OH$ . This suggests that the compounds act differently on the fungus. The fungicide chemist, therefore, has a biological tool to tell him whether he is making progress down a new road or only farther along the old road. Secondary screening techniques involve fungus, chemical, and host. See also *Antiseptics (testing)*.

At present there are three major groups of fungicides: heavy metals, elemental sulfur and polysulfides, and organic compounds. Each of these will be discussed in order.

### Heavy-Metal Fungicides

Much research has been done to discover the best heavy metal for use in fungicides. None has yet proved generally superior to copper. Copper has many advantages. It is widely toxic to fungi, and not widely toxic to host plants nor to humans. It is reasonably cheap, and forms types of salts that resist rain and other weather factors. See *Copper compounds*.

The fungicidal action of copper was discovered late in the 18th century when copper sulfate was used to treat wheat seed to kill the spores of the smut fungus. Its use was not extended to foliage for another hundred years because copper sulfate was toxic to foliage. Late in the 19th century, a Frenchman of Bordeaux discovered that the black-rot disease of grape was absent from foliage treated with an unpleasant-looking mess of copper sulfate and lime applied to prevent pilferage. Lime (calcium hydroxide) antidoted the injurious action of copper sulfate on foliage and Bordeaux mixture was born. Bordeaux mixture, which has probably saved more food for the world than any other pesticide discovered prior to DDT, is a chemist's nightmare. Page has been piled on page of reports discussing the chemistry of the mixture. At first, the reaction was believed to be simple:





but many later chemical studies threw doubt upon this interpretation (9). The chief difficulty is that 25 per cent less calcium hydroxide is required than indicated from stoichiometric considerations. This result leads most investigators to write the formula for the final mixture as  $4\text{CuO} \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$ . There is some doubt as to the degree of hydration, however. This compound may be described as copper trioxysulfate or more commonly as tribasic copper sulfate. Martin has returned to the original formula contending that the  $\text{Cu}(\text{OH})_2$  is stabilized by the calcium sulfate (9).

A few "ready-made" basic salts of copper have been introduced to compete with Bordeaux mixture as sprays. They have the distinct advantage of freedom from lime, which is toxic to many vegetable plants. At various times, copper silicate, copper zeolite, cuprous oxide, copper oxychloride, tribasic copper sulfate, and a double salt of basic copper chloride and basic sulfate have been used. These copper compounds are rapidly disappearing from the vegetable and potato fields with the rise of dithiocarbamate salts. The last two are still used extensively on cherries, however. Copper carbonate and cuprous oxide are the important "ready-made" compounds of copper that are used as seed treatments. Copper carbonate has had a wide and long-continued use as a treatment for the stinking smut disease of wheat since its original proposal by Darnell-Smith in 1917. In recent years, the trend has been toward replacing the copper carbonate with organic mercury materials. Cuprous oxide was introduced by Horsfall in 1932 as a vegetable-seed treatment. Its use rapidly expanded during the 1930's on such crops as spinach, peas, beets, and tomatoes. Its use declined just as spectacularly in the 1940's following the discovery of the fungitoxic action of chloranil in 1938 and the introduction of tetramethylthiuram disulfide by Tisdale. Cuprous oxide also has been widely used as a foliage spray, but the usage is declining.

Mercury has had a long vogue in plant pathology. Corrosive sublimate (mercuric chloride,  $\text{HgCl}_2$ ) still is used extensively on seeds. Riehm, the German plant pathologist, following Ehrlich's work on organic arsenic for syphilis, developed *o*-(chloromercuri)phenol,  $\text{C}_6\text{H}_4(\text{OH})\text{HgCl}$ , for seed treatment, and this was followed by other organic mercury compounds, notably ethylmercuric chloride,  $\text{C}_2\text{H}_5\text{HgCl}$ , ethylmercuric phosphate, and phenylmercuric cyanamide. These are or have been widely used in seed treatment especially against the cereal smuts. 2-Chloro-4-(hydroxymercuri)-phenol was one of the first recognized seed protectants. A coating over the seed prevents attack by soil fungi. Zinc 2,4,5-trichlorophenate,  $(\text{C}_6\text{H}_2\text{Cl}_3\text{O})_2\text{Zn}$ , is finding a place in the seed treatment of cotton for seed- and soil-borne diseases.

Owing to the rise of organic fungicides in the 1940's, the heavy-metal compounds have tended to drop into the background. Harry and his co-workers have used non-Daltonian complexes of chromium and other metals (3). The chemistry of these materials is unusual, for they seem to be intermediate between true molecular compounds and mechanical mixtures. A complex of copper, zinc, and chromium (hexavalent) shows promise as a potato fungicide, but it has as yet received little commercial adoption. Another complex, containing most of the heavy metals ever investigated as fungicides, has the composition  $6\text{CdO} \cdot 100\text{CaO} \cdot 25\text{CuO} \cdot 10\text{ZnO} \cdot 25\text{SO}_3 \cdot 10\text{CrO}_3 \cdot 170\text{H}_2\text{O}$ . This seems to be specific for turf diseases. Its success has stimulated further search for cadmium compounds.

### Sulfur and Calcium Polysulfide

Sulfur has been used as a fungicide since the times of Homer, at least. It is quite toxic to many fungi, not very toxic to higher plants, and hardly toxic at all to warm-

blooded animals. It is very insoluble, resistant to light, but rather weak in capacity to cling to treated tissue. For practical use sulfur must be made "wetttable" by means of various surface-active compounds. If it is rendered too wetttable, it washes off the plant too easily; if not enough, it rises to the top of the spray tank and does not pass through the pump. Moreover, the particle size must be small if the sulfur is to perform satisfactorily. One answer to these problems that prevailed for a hundred years was known as "lime sulfur." Lime sulfur is prepared by boiling sulfur and calcium oxide together to form calcium polysulfides, which may be represented  $\text{Ca}=\text{S}_x=\text{S}$ . This substance, consisting of mixed polysulfides, is much more toxic to spores than elemental sulfur and it is likewise much more toxic to the host plants. Lime sulfur on standing decomposes giving elemental sulfur with a very minute particle size, which resists rainfall better than "wetttable sulfur." Sulfur finds its most successful use on rosaceous plants like apples and other noncitrus fruits. It is a less active fungicide than copper, but the phytotoxicity is so much lower that it is preferred. Sulfur largely replaced Bordeaux mixture on fruit in the early part of the 20th century.

### Organic Fungicides

The first successful organic fungicide was formaldehyde (*q.v.*), which was put forward in the 1890's as a treatment for seed of the white potato. On a molar basis it is a rather low-grade toxicant, but its volatility is an advantage in soil fumigation, because the toxicant disappears from the soil and the seeds can then be planted. Formaldehyde is also used for fumigating storage houses. Formerly, it had some use as a seed treatment. Chloropicrin (*q.v.*),  $\text{CCl}_3\text{NO}_2$ , has also been used for a soil fumigant. It is much more active than formaldehyde.

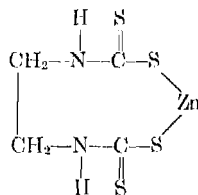
The first organic fungicide for foliage was ferric dimethyldithiocarbamate,  $[(\text{CH}_3)_2\text{NCSS}]_3\text{Fe}$ , the first of a long series of dithiocarbamates, some of which enjoy wide popularity as foliage protectants. The specificity of these compounds for different diseases is striking. The basic synthesis for the group is the reaction of the proper amine with carbon disulfide in the presence of an alkali. The simplest example is sodium dimethyldithiocarbamate,  $(\text{CH}_3)_2\text{NCSSNa}$ , which is produced as follows:



Sodium dimethyldithiocarbamate is a good spore killer but it is of no value on foliage because it is so soluble that it washes off in the first rain. The ferric salt is much used as a spray for the scab and rust diseases on apples, for it seems almost to be a specific for rust diseases. It is also used for blue mold of tobacco. The compound is tenacious and stable. Its coal-black color detracts somewhat from the success of the compound because it downgrades the fruit. The zinc salt,  $[(\text{CH}_3)_2\text{NCSS}]_2\text{Zn}$ , cannot be used on apples because of fruit russetting due to the zinc. Compounds of this type seem to be specific for the anthracnose group of diseases. Many other metallic salts of the dimethylamine derivatives have been tried, but none has been as successful as the iron and zinc salts.

A more recent introduction in the dithiocarbamate field is disodium ethylenebis-dithiocarbamate,  $\text{NaSSCNH}(\text{CH}_2)_2\text{NHCSSNa}$ . This compound is by far the most fungitoxic on the molar basis of any dithiocarbamate so far produced. It is made from ethylenediamine instead of dimethylamine. Although the compound is water-soluble, it has a curious capacity to cling to a treated surface and resist rainfall. This is about the only fungicide so far known with that property. Disodium ethylenebis-

dithiocarbamate reached the stage of commercial adoption despite being very unstable. The compound would probably have been abandoned had not a lucky accident resulted in showing the value of zinc sulfate in stabilizing the compound (4). In present practice, a slight molar excess of zinc sulfate is added to the spray tank just before use. The probable structure of the zinc salt is:



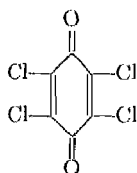
Despite their close similarity in composition and even in structure, zinc ethylenebis-dithiocarbamate and zinc dimethyldithiocarbamate have decidedly different fungicidal properties. Zinc ethylenebisdithiocarbamate has a much wider range of fungitoxic action than zinc dimethyldithiocarbamate. Thus the former will control both the *Alternaria* target spot and the *Phytophthora* late blight of tomato; the latter will control only the target-spot disease. Presumably the two compounds affect different biological systems. Tank-mixed zinc ethylenebisdithiocarbamate is rapidly replacing copper compounds on the potato crop. The compound seems almost specific for the diseases of potato and tomato.

A fungicide related to the dithiocarbamates is tetramethylthiuram disulfide,  $[(\text{CH}_3)_2\text{NCSS}]_2$ . This compound is an excellent foliage spray, but it is much more expensive than the dithiocarbamates and hence is seldom used on foliage except on turf for the brown-patch disease. It has found a place for itself as a dust seed treatment for vegetable and corn seeds. It has the disadvantage of being a skin irritant, to such an extent that workmen have refused to use it. However, a machine has been invented to treat seeds with a slurry of the compound, and in this manner the irritant effects are avoided.

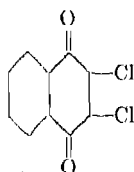
Chloranil (I), tetrachloro-*p*-benzoquinone, is a powerful fungicide. It may be significant that it is a pro-oxidant; copper can act as a pro-oxidant, and the compound was selected for testing on the hypothesis that there may be a connection between pro-oxidant action and fungicidal action. The compound turned out to have especially desirable qualities as a seed protectant for legume seeds. It prevents their decay by soil-borne microorganisms. Considering that the compound is used at the low dose of 0.25% by weight of seed (depending upon size), the tonnage sold is impressive. The compound practically drove copper out of the field for seed protection. Chloranil is not satisfactory as a foliage spray, presumably because it undergoes photochemical oxidation to chloranilic acid which is soluble and washes off. The compound must be limited to seed treatment where it can remain in the dark.

The only other commercial quinone fungicide is 2,3-dichloro-1,4-naphthoquinone (II). It shows a very wide range of fungitoxicity and gives field control of a variety of fungus diseases. It seems to be the least specific in its action of any of the new organic fungicides. It promises to reach the stage of large-scale commercial adoption on apples, especially in the northern apple belts. On the other hand, the compound shows more tendency toward phytotoxicity than the others. It gives excellent control, for example, of the dreaded late blight disease of potatoes, but at the same time may reduce the yield of potatoes. The compound seems to affect the physiology of the

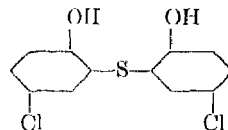
potato plant so that the starch made in the leaves does not move to the roots to make tubers. It may produce some speckling of leaves and fruits of apples. It has been claimed that some of this injury may be avoided by adding magnesium sulfate to the spray fluid. Another serious disadvantage is the skin rash produced on some operators by the compound.



(I) Chloranil



(II) 2,3-Dichloro-1,4-naphthoquinone



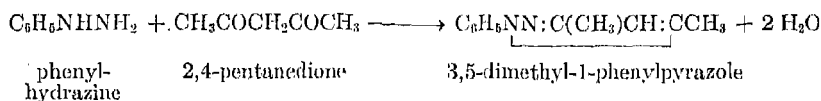
(III) 2,2'-Thiobis(4-chlorophenol)

Heterocyclic compounds known variously as imidazolines or glyoxalidines, obtained by reaction of ethylenediamine with fatty acids, were introduced by Wellman and associates (12). The most promising member of the series so far appears to be 2-n-heptadecylglyoxalidine,  $\text{NHCH}_2\text{CH}_2\text{N:CC}_{17}\text{H}_{35}$  (see *Ethylene amines*). It is

used commercially for leaf spot on cherries and has been tested on a large scale for scab on apples.

Next to sulfur, nitrogen appears to be the most important constituent element of an organic fungicide (other than carbon and hydrogen, of course). Often this nitrogen occurs in a heterocyclic system. Chlorination of organic compounds seems to be much less important in fungicides than in insecticides. Perhaps the earliest heterocyclic-nitrogen fungicide was 8-quinolinol (8-hydroxyquinoline),  $\text{HOC}_9\text{H}_6\text{N}$ , and 8-quinolinol sulfate. The sulfate is not used to protect foliage because it is too soluble, but it has found some use as an internal fungicide (chemotherapeutant) for Dutch elm disease (1). In the mid-thirties the French plant pathologists recommended the copper complex of 8-hydroxyquinoline for foliage use. Recently, the compound has been reintroduced in America for the purpose. Its probable commercial adoption is small, however, because of cost and because the copper is toxic to copper-sensitive plants.

In late 1949, McNew and Sundholm published on the fungicidal action of pyrazole derivatives (10). The compounds are typically prepared by treating hydrazine or phenylhydrazine with a  $\beta$ -diketone compound as follows:



Substitution of a nitroso group in the 4-position enhances the activity of the pyrazole, especially when the molecule also contains an aryl group in the 1-position. These compounds are said to be probably "the most effective organic fungicides revealed to date." Chemically, it is interesting to note the similarities to the glyoxalidines. In both cases we have 5-membered rings with two nitrogens in the ring. In the pyrazoles the two nitrogens are joined; in the glyoxalidines they are separated by a carbon atom. On the basis of present data, the two types cannot be said to act similarly on the biological systems of the fungi. Pyrazoles probably will not become commercially important until some way is found of eliminating the serious hazard of skin irritation pre-

sented by all those that have been tested up to the present. 2-Aminopyridine,  $\text{NH}_2\text{C}_5\text{H}_4\text{N}$ , has recently been mentioned as a possible compound for dipping picked oranges to prevent rot in storage and transit.

Quaternary ammonium compounds (*q.v.*) depend apparently for their fungicidal action on the presence of tetravalent nitrogen, either in a straight chain or as a hetero-atom in a ring system. An example is laurylisoquinolinium bromide, which has a very high fungistatic level but, together with other quaternary ammonium compounds, is too soluble in water to be effective as a protectant. The only quaternary ammonium compound that has found practical use in agriculture is mercuric triethanol-ammonium lactate. This compound, although water-soluble, has some protective value. Probably its success lies, however, in its ability to penetrate diseased leaf spots and kill out the infecting fungus, thus curing the leaf.

Diphenyl, like most hydrocarbons, has only a negligible fungitoxicity. Occasionally, it has been used to dip oranges to prevent rot in storage. The insertion of bridges between the rings seems to add little to the fungitoxicity, but hydroxyl or amine substitutions in the rings add toxicity. 2,2'-Dihydroxy-5,5'-dichlorodiphenylmethane (2,2'-methylenebis(4-chlorophenol)) has been used as a mildew-proofer of military material (8), but it seems to have little possibility for plant-disease control. If, however, a sulfur bridge is substituted for the methane bridge between the two rings, a potent fungicide for apple scab appears, 2,2'-thiobis(4-chlorophenol) (III). This compound has not yet reached the stage of commercial adoption. In some tests the compound russets the apple fruit.

### Biological Activity of the Compounds

If ever the development of fungicides is to emerge from its present empirical fog, more knowledge of the biological activity must be obtained. A brief summary of present knowledge follows: Three basic types of action are postulated at present, protein precipitation, interference with enzyme systems, and antagonism of essential metabolites in the cell. The compounds which presumably act in these three ways are: (1) protein precipitation—formaldehyde, heavy metals; (2) interference with sulfhydryl enzymes—heavy metals, quinones; interference with metal-containing enzymes—sulfur, hydrogen sulfide, dithiocarbamates, probably other organic sulfur compounds, hydroxyquinoline derivatives, and any other nitrogen compound capable of forming chelate complexes with metals; (3) interference with essential metabolites—quinones, copper, nitroso pyrazoles and other strong oxidants, which probably interfere with oxidation-reduction systems involving such compounds as cysteine, and ascorbic acid. Horsfall and Zentmyer (6) showed that most reagents for aldehydes, sugars, amines, or amino acids were fungitoxic.

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## INDUSTRIAL FUNGICIDES

Fungicides for the sterilization and preservation of industrial products have not had as long a history as those used for combating plant diseases, nor has the study of industrial fungicides been as intensive. Most of the compounds currently in use are of recent development and represent stop-gap measures awaiting new and more effective fungicides. A compilation of industrial fungicides is a heterogeneous conglomerate. Relatively few are generally applicable for a diversity of items, as is the case with Bordeaux mixture in plant pathology and DDT in insect control. The chief cause for the restricted application of a given industrial fungicide lies in the varied nature and end uses of the respective items involved. Often the secondary properties of the fungicide under consideration, such as toxicity to humans, reaction with metals, leaching by rain, catalytic effect on actinic degradation, incompatibility with other compounds on the material, cost, and ease of application, weigh as heavily as the ability to inhibit microbiological growth per se. For this reason the principal compounds in use today as industrial fungicides are here grouped according to the industrial products involved, rather than according to the chemical nature of the fungicide. See also *Food chemicals*.

**Adhesives.** Synthetic resin adhesives such as urea-formaldehyde are relatively resistant to fungal attack. Adhesives and glues of starch, casein, dextrin, or bone origin are extremely susceptible. For the inhibition of microbiological growth in this group,  $\beta$ -naphthol,  $C_{10}H_7OH$ , in concentrations of approximately one per cent is fairly satisfactory. Organic mercurials,  $RHgX$ , have also been suggested. In this case, however, particular care must be exercised on account of their human toxicity, and they should not be used in adhesives for gummed labels or items which come into continuous or intimate contact with the skin.

**Air.** Many compounds have been investigated for the control of acute respiratory infections in industry by reducing the number of air-borne pathogenic microorganisms. Although these organisms are in most cases bacterial rather than fungal, the subject may well be considered here. Sprays of glycols, lactic acid, and hypochlorous acid have been developed. Propylene glycol,  $CH_3CHOHCH_2OH$ , is used in concentrations of approximately 1 gram per 3000 liters of air. Although this compound is not toxic to man at a concentration of 0.3 mg. per liter for several hours' exposure, the treated air is characterized by a stale and unpleasant odor. The glycol also condenses on the walls and windows, leaving a sticky film. Triethylene glycol,  $(HOCH_2CH_2OCH_2)_2$ , is a more effective disinfectant than propylene glycol, and is also superior in that it does not condense as readily on the walls. With both compounds, however, the treated air is uncomfortable to patients during warm weather. Despite the effectiveness of glycolization in lowering the bacterial count in air, there are not sufficient rigorous data

at the present time to make a definite statement as to the desirability of these disinfecting treatments. See *Air conditioning*.

**Cork.** Resin-bonded cork is far less susceptible to microbiological growth than glue-glycerol-bonded cork. For the latter case, one of the most effective fungicides available is *p*-nitrophenol,  $\text{C}_6\text{H}_4(\text{NO}_2)(\text{OH})$ . This is added in concentrations of about 2%. Salicylanilide, zinc dimethyldithiocarbamate, and 2,2'-methylenebis(4-chlorophenol) have also been used but so far found to be less effective. All of these compounds can be applied either in organic solvents or paraffin waxes.

**Cotton Fabrics and Cordage.** During the 1940's, over a thousand compounds were tested as possible fungicides on cotton fabrics and cordage. Many have been found satisfactory for suppressing the mildewing of fabrics during storage or shipment. Of these, the most popular has been salicylanilide,  $\text{HOC}_6\text{H}_4\text{CONHC}_6\text{H}_5$ , which has the advantage of being colorless and odorless. It can be applied either from organic solvents or in the form of its sodium salt in aqueous solutions. A final concentration of 0.1–0.5% based on the weight of the cloth is usually sufficient. Pentachlorophenol, tetrachlorophenol, and their sodium salts are also satisfactory for this purpose. However, when the treated fabrics are used outdoors, subject to the rain, sunlight, and wind, or in contact with the ground, these fungicides are nondurable and ineffective. The two compounds at present preferred are copper naphthenate and the copper derivative of 8-hydroxyquinoline. Copper naphthenate (see *Driers and metallic soaps*) displays good fungicidal action at concentrations of about 0.5%. It is applied either from organic solvents or aqueous emulsions. Because of its unpleasant odor, dark green color, skin irritation, tackiness, and deteriorative effects on certain metals, the use of copper naphthenate has been restricted to areas where these disadvantages are not important considerations. Although not as effective from a purely mildew-proofing viewpoint, zinc naphthenate has been used to overcome some of these objections.

The most promising compound emerging from the extensive testing program carried out during World War II is the copper derivative of 8-hydroxyquinoline,  $\text{Cu}(\text{OC}_9\text{H}_6\text{N})_2$  (see *Quinoline*). This compound is odorless, light yellowish green, and highly insoluble in most solvents. For some time the insolubility of the compound has been an underlying difficulty in application techniques in ordinary textile mills. Recently, however, the compound has been put into solution by the addition of solubilizing agents, and its use has become widespread. When added to cotton fabrics in concentrations of 0.1–0.5%, it provides high antimildewing activity in outdoor exposures.

Other popular fungicides include cuprammonium hydroxide, phenyl mercurials, pyridyl mercurials, trimethyloctadecylammonium pentachlorophenate, and 2,2'-methylenebis(4-chlorophenol).

**Leather.** In the preservation of skins for museum purposes, soaking for 15–30 minutes in a 1% solution of sodium fluosilicate,  $\text{Na}_2\text{SiF}_6$ , will stop bacterial growth on freshly flayed skin. Phenylmercuric acetate,  $\text{C}_6\text{H}_5\text{HgOOCCH}_3$ , and other phenyl mercurials are similarly used in the tanning industry to stop microbiological decay in the cure and soak water. As a class, the phenyl mercurials are stable compounds. Their solubility is dependent largely on the anion. Thus, the oleate and stearate are much more soluble in nonpolar solvents than the acetate and chloride. The organic mercurials are more corrosive to galvanized iron and aluminum than other fungicides and will cause blistering on human skin if not washed off. For the prevention of

mildewing on finished leather other compounds have been employed. So far the most suitable are the copper complex of 8-hydroxyquinoline and *p*-nitrophenol, either alone or in combination with pentachlorophenol. The compounds can be applied either in shoe waxes or from organic solutions. A typical formulation for the purpose is: 2% *p*-nitrophenol, 2% pentachlorophenol, 10% neatsfoot oil, 16% cyclohexanone, and 70% perchloroethylene.

**Lenses and Prisms.** In the tropics, fungi have been known to etch lenses and prisms in optical equipment. The growth can be controlled through the use of radium foil in the form of a collar around the lens in binoculars and transits. However, the relative scarcity and high cost forced this method of protection to give way to other fungicides. Short-term protection has been given by *m*-cresyl (*m*-tolyl) acetate,  $\text{CH}_3\text{C}_6\text{H}_4\text{OOCCH}_3$ , and ethylmercuric thiosalicylate,  $\text{C}_2\text{H}_5\text{HgOOCCH}_2\text{CH}_2\text{SH}$ . Because of their deteriorative effects on metals, however, these two compounds must be used in small concentrations.

**Paints and Lacquers.** Fungi grow well under humid conditions on linseed oil- and casein-based paints. Local discoloration results, which may become widespread. Phenylmercuric oleate,  $\text{C}_6\text{H}_5\text{HgOOC}(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{CH}_3$ , appears to be the best antimildewing agent for house paints to date. As low as 0.02% mercury by weight is sufficient. Other compounds that have been studied include phenylmercuric acetate, phenylmercuric naphthenate, chlorinated phenols, salicylanilide, zinc dimethyldithiocarbamate, and the copper complex of 8-hydroxyquinoline. Actually, in many cases the pigments themselves, such as zinc, copper, lead, and chromium oxides, are effective fungicides.

**Pharmaceuticals and Cosmetics.** Alcohol exerts a good preservative action in pharmaceutical preparations in concentrations above 15%. The same action is exhibited by 50% glycerol and 50% sucrose solutions. Frequently, when these are absent or present in lower concentrations, antimicrobial agents are added; the glycerol  $\alpha$ -ether of *p*-chlorophenol is an example. Its use is limited, however, by its lingering burning taste to nonoral uses. Alkyl and benzyl esters of *p*-hydroxybenzoic acid in concentrations of 0.05–0.15% are more widely used, particularly in cold creams, lotions, hair-waving fluids, and soaps. Others employed include eugenol, propylene glycol, phenylmercuric nitrate, phenol, and cresol derivatives.

**Plastics.** Synthetic polymers themselves are not susceptible to attack by fungi and bacteria. Many of the plasticizers used in formulating plastic materials, however, are excellent supporters of microbiological growth. This is particularly true of fatty acid esters and castor-oil derivatives. In such cases, attempts have been made to prevent microbiological growth by the addition of fungicides. So far there is no compound adopted for wide general use. Laboratory results reported by various workers indicate promise in the organic mercurials and the copper derivative of 8-hydroxyquinoline.

**Water.** The principal agent used in water purification is chlorine, which is added either as the free liquid or as calcium and sodium hypochlorites. For the purification of drinking water between 3–8 pounds of chlorine per million gallons of water is usually sufficient. Sometimes ammonia is added just before the chlorine in weight ratios of 1:4 for the purpose of decreasing the unpleasant taste of chlorine. In swimming pools the amount of free chlorine is kept below 0.5 p.p.m. Chlorine is noticeable in concentrations of 10 p.p.m. in air and becomes irritating to the lungs and membranes of the nose and throat with increasing concentrations. Its germicidal effect is influenced by



many factors. Alkaline conditions as well as the presence of sulfur or iron suppress its activity.

On a much smaller scale and for small volumes of water, Halazone (*p*-dichloro-sulfamylbenzoic acid) and succinylchlorimide have been employed. The former does not impart an evident taste even at concentrations of 4 p.p.m. Diglycine hydroiodide, bromides, and silver preparations have also been tried, although with less success. Quaternary ammonium derivatives, such as Phomerol chloride (benzyltrimethyl- $\{2-[2-(p-1,1,3,3\text{-tetramethylbutylphenoxy})\text{ethoxy}]\text{ethyl}\}$  ammonium chloride), are quite satisfactory in disinfecting drinking water for poultry in concentrations of 1 p.p.m. See also *Water, industrial and municipal*.

**Wood.** Coal-tar creosote has been the standard preservative, particularly for railroad ties. It is a distillate from coal tar boiling between 200 and 400°C. and is made up of a host of hydrocarbons and heterocyclic derivatives. Compounds identified in creosote include cresols, naphthols, toluene, benzene, phenanthrene, fluorene, pyridine, and quinoline. The mixture is applied most effectively by tank dips, either in the open or under pressure. It can also be painted or sprayed onto the wood. Railroad ties have a life expectancy of 5.5 years, but this is increased fivefold by creosote treatment.

Less effective are water-soluble derivatives, the principal one in the U.S. being zinc chloride. Because of its ready leachability by water, attempts have been made to increase its durability. Chromated zinc chloride is one of the chief products from this development. This is a mixture of 4 parts of zinc chloride to 1 part of sodium chromate. Sodium fluoride, copper sulfate, mercuric chloride, and arsenic salts have also been tried in a minor way.

Organic compounds applied from 5% solution in organic solvents include tetra- and pentachlorophenol, chloro-*o*-phenylphenol, and  $\beta$ -naphthol. The effectiveness of these treatments is difficult to assess at the present time in view of the insufficiency of service records. In general, they are not as efficient as creosote from a preservative standpoint. However, there are uses in which the ready flammability, the objectionable odor, the stickiness, the toxicity, and the incompatibility with paints of creosote are highly undesirable. In such cases, some of these compounds may find quite a demand. Frequently, mixtures are preferred. A typical treatment of this kind is the hot-bath dip for telephone poles. The poles are soaked for several hours in hot creosote, followed by a similar length of time in a cold bath of 5% pentachlorophenol in a 4:1 mixture of petroleum and creosote.

**Wool** is as rapidly digested by microorganisms as cotton, particularly by species pathogenic to man. So far, relatively few investigations have been carried out on the mildew-proofing of woollen fabrics. Slime resulting from bacterial growth on paper-makers' felt is effectively controlled by a 12-hour soaking in phenylmercuric acetate or chlorinated phenol solutions. Mixing of copper oleate in the paper pulp itself is another technique employed for the same purpose. For felt gaskets, copper pentachlorophenate, phenylmercuric oleate, the copper derivative of 8-hydroxyquinoline, 2,2'-methylenebis(4-chlorophenol), and zinc dimethyldithiocarbamate have shown considerable promise in concentrations of about 1%.

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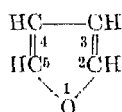
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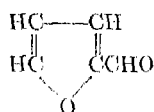
**FURAL, 2-FURALDEHYDE**,  $C_4H_3OCHO$ . See *Furfural*.**FURAN**,  $O.CH:CH.CH:CH$ . See *Furfural*.**FURANOSSES**. See *Carbohydrates*, Vol. **2**, p. 874.**FURFURAL AND OTHER FURAN COMPOUNDS**

Furfural.....	p. 996	Furan.....	p. 1004
Furfuryl alcohol.....	1002	Tetrahydrofuran.....	1005
Tetrahydrofurfuryl alcohol.....	1003	Furoic acid.....	1006

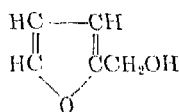
Furfural is the most important of the compounds containing the five-membered furan ring (*R.I.* 111) (I), characterized by one oxygen atom. It is an aldehyde (II) with the  $-CHO$  group in the 2(or  $\alpha$ )-position, and it is obtained on a large scale from



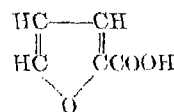
(I) Furan



(II) Furfural

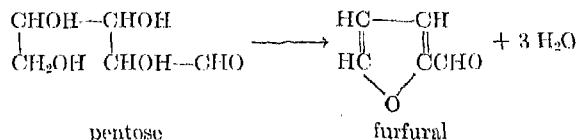


(III) Furfuryl alcohol

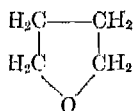


(IV) Furoic acid

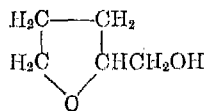
corncocks, oat hulls, cottonseed hulls, and other agricultural residues containing pentosans, which yield pentoses on hydrolysis:



The corresponding alcohol, furfuryl alcohol (III), and acid, furoic acid (IV), as well as furan itself are also commercial products. More important in commercial volume than the acid and furan, however, are two saturated derivatives, tetrahydrofuran (V) and tetrahydrofurfuryl alcohol (VI).



(V) Tetrahydrofuran



(VI) Tetrahydrofurfuryl alcohol

The polyfunctional nature of the furan nucleus, which may be considered a dienic ether, leads to an interesting group of reactions. This nucleus, with its conjugated unsaturation, is usually classed as aromatic and possesses a relatively high order of stabilization due to resonance. Substitution takes place preferentially in the  $\alpha$  (2 or 5)-positions. However, the aromatic character of the furan nucleus is very weak, as shown by its ability to undergo additions almost as readily as an aliphatic diene such as vinyl ether or butadiene. Thus furan, alkylfurans, and the simple halofurans, among others, react readily with maleic anhydride to form the expected Diels-Alder adducts, 3,6-endoxotetrahydrophthalic anhydrides (31). Furthermore, furan and alkylfurans are susceptible of hydrolytic fission. 2,5-Dimethylfuran, for example, on hydrolysis in aqueous acetic acid in the presence of a little sulfuric acid yields 88% of acetonylacetone (2,5-hexanedione),  $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3$ . Ring opening can also be effected by catalytic oxidation in the vapor phase.

### Furfural

Furfural (2-furaldehyde (C.A.), fural, 2-furancarboxaldehyde, furfuraldehyde, furole),  $\text{C}_5\text{H}_4\text{OCHO}$ , formula weight 96.08, is a water-white liquid when freshly distilled, but darkens on standing in contact with air. The principal uses for furfural are as an intermediate in the manufacture of hexamethylenediamine (employed in the manufacture of nylon), and compounds containing the furan ring (including furfuryl alcohol, tetrahydrofurfuryl alcohol, furan, and tetrahydrofuran); as a selective solvent for separating saturated from unsaturated compounds in petroleum lubricating oil, gas oil, and Diesel fuel, as well as vegetable oil; as an ingredient in resins, especially of the phenol-aldehyde types; as a decolorizing agent for wood rosin; as a resin solvent and wetting agent in the manufacture of abrasive wheels and brake linings; and in the extractive distillation of butadiene and other  $\text{C}_4$  hydrocarbons for the manufacture of synthetic rubber.

The discovery of furfural is credited to Dobereiner, whose work was first reported in 1832. During the next 90 years, about 2000 investigations were reported in the literature, but in 1920 there was still no commercial production of furfural. During research undertaken in that year to produce an improved live-stock feed by acid-digesting oat hulls, Brownlee discovered furfural in the vapors from the digester (3). The first drum of furfural was produced by The Quaker Oats Company in February 1922, at Cedar Rapids, Iowa, and the first important commercial use of furfural was by Stokes and Smith Company (now Borden Company) for the production of phenolic resin. Other uses were soon developed, and the demands for furfural of the synthetic rubber program during World War II, added to other wartime demands, made necessary a considerable expansion in production capacity. Laboratory work on furan compounds has continued apace, and today there are some 4000-5000 scientific articles as well as some 3200 patents on furan compounds or their applications. About one-sixth of these patents deal with resins in some form.

### PHYSICAL AND CHEMICAL PROPERTIES

*Constants.* Some of the physical properties of furfural and other furan compounds are given in Table I. Additional properties of furfural are as follows: vapor pressure:

Temperature, °C. ....	39.9	92.3	120.3	131.6	140.2	154.4	159.0	160.9	163.8	170.6
Vapor pressure, mm.										
Hg. ....	8	69	214	310	411	625	707	744	812	966

viscosity at 38°C., 1.35 centipoises, at 54°, 1.09 centipoises, at 99°, 0.68 centipoise; heat of vaporization at 160.6°C., 10,321 gram-cal./gram-mole; heat of combustion, 560.3 kg.-cal./gram-mole; lower explosive limit at 125°C., 2.1 vol. % in air; coefficient of expansion, 0.00110/°C.; ignition temperature, 315–57°C.; dielectric constant at 25°C., 38.0. Figure 1 shows vapor-liquid compositions for the furfural-water system.

TABLE I. Physical Properties of Some Furan Compounds.

Property	Furfural	Furfuryl alcohol	Tetrahydro-furfuryl alcohol	Furan	2-Methyl-furan	Tetrahydro-furan
Formula wt.	96.08	98.10	102.13	68.07	82.098	72.10
M.p., °C.	–36.5	–14.63	—	–85.68	–88.68	–108.5
B.p., °C.	161.7	171.0 <sub>750</sub>	177.5 <sub>743</sub>	31.3	62.5–64.5	65–67
$d_4^{20}$	1.161 <sub>20</sub>	1.135 <sub>20</sub>	1.064 <sub>20</sub>	0.937	0.914	0.887
$n_D^{20}$	1.526	1.486	1.4505	1.4214	1.434	1.407
Surface tension at 25°C., dynes/cm.	49.0 <sub>20</sub>	38.2	36.5 ± 0.5	—	—	—
Viscosity at 25°C., centipoises	1.49	4.62	5.49	—	—	—
Flash point (open cup), °C.	56.8	75.0	75–80	–40	–30	–17.2

At pressures above atmospheric, the vapor-liquid equilibrium curve is pulled in toward the 45° line. Curtis and Hatt give data for furfural-water mixtures at 72, 97, and 125 p.s.i. (9). Table II gives the mutual solubilities of furfural and water (32). For solubilities of various organic compounds in furfural see references (32) and (34).

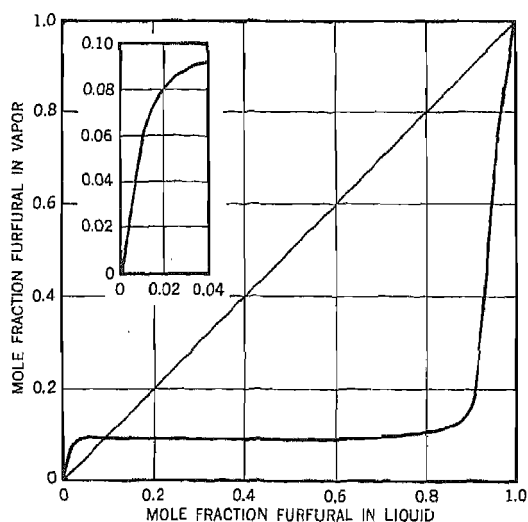


Fig. 1. Vapor-liquid compositions, furfural-water.

**Reactions.** While pure furfural is a colorless liquid, industrial furfural is light yellow to brown in color. It is normally handled and stored in iron or steel equipment without any special precautions, although there is a gradual darkening of color and increase in acidity and polymer formation when furfural is stored in contact with air. This autoxidation can be prevented by storing in an oxygen-free atmosphere (13).

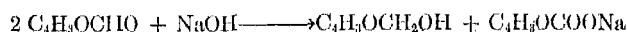
TABLE II. Mutual Solubility of Furfural and Water.

Temp., °C.	Furfural, wt. %		Temp., °C.	Furfural, wt. %	
	Water layer	Furfural layer		Water layer	Furfural layer
10.....	7.9	96.1	60.....	11.7	91.4
20.....	8.3	95.2	70.....	13.2	90.3
30.....	8.8	94.2	80.....	14.8	88.7
40.....	9.5	93.3	90.....	16.6	86.5
50.....	10.4	92.4	97.9 <sup>a</sup> .....	18.4	84.1

<sup>a</sup> Boiling point at 760 mm.

Furfural has a high order of thermal stability in the absence of oxygen (11). At temperatures as high as 230°C., exposure for many hours is required to produce detectable changes in the physical properties of furfural, with the exception of color. Furfural losses in solvent refining of lubricating oil and in the extractive distillation of butadiene are very low (see pp. 1001, 1002).

The chemical reactions of furfural are a combination of those of the aldehyde group (see *Aldehydes*) and those of the furan nucleus. It can be oxidized to furoic acid, reduced to furfuryl alcohol, and converted to furan by passing its vapors with steam over catalysts (39). With strong alkalis like sodium hydroxide furfural undergoes the Cannizzaro reaction, yielding furfuryl alcohol and sodium furoate:



In the presence of sodium cyanide, it condenses with itself to form *furoin*,  $\text{C}_4\text{H}_3\text{OCH(OH)COC}_4\text{H}_3\text{O}$ , m.p. 134–35°C., the furan analog of benzoin (20), which is readily oxidized to *furil* (bipyromucil),  $\text{C}_4\text{H}_3\text{OCOCOC}_4\text{H}_3\text{O}$ , m.p. 165–66°C. With ammonia, hydrofuranide is obtained, paralleling the conversion of benzaldehyde to hydrobenzamide (see Vol. 2, p. 415). Like other aldehydes, furfural condenses with compounds possessing active methylene groups, such as aliphatic carboxylic esters and anhydrides, ketones, aldehydes, nitriles, and nitroparaffins (16, 22), and with phenols to form resins.

The negative character of the aldehyde group in furfural renders the furan nucleus less susceptible to hydrolytic fission than is the case with alkylfurans. Even at high temperatures, long exposure is required to bring about extensive destruction of furfural by dilute acids (35). Formic acid and a black resin are the products of destruction by this means, the reaction rate being dependent upon the concentration and strength of the acid catalyst. The nucleus is susceptible to attack by atmospheric oxygen, leading to acidic autoxidation products, but this reaction may be inhibited by the addition of catalytic amounts of basic materials such as tertiary amines (10,13). Catalytic vapor-phase oxidation of furfural yields maleic acid (29).

Since nuclear substitution reactions preferentially introduce a substituent at an  $\alpha$ -carbon atom, furfural yields the corresponding 5-nitro-, 5-chloro-, and 5-bromo-substituted aldehydes (8,17,18). The nucleus in furfural is less dienic in character than in furan, and this aldehyde fails to give an adduct with maleic anhydride. However, at elevated temperatures, two moles of butadiene add to one of furfural by what appears to be a Diels-Alder-type reaction (21) in which the aldehyde takes the dienophile role.

#### METHODS OF ANALYSIS

Furfural forms the usual aldehyde derivatives (phenylhydrazone, m.p. 97°C.; semicarbazone, m.p. 202°C.) and these may be used for identification purposes. A

quick qualitative test may be made by adding a few drops of a solution of aniline in glacial acetic acid to an aqueous solution of furfural (37). An intense red color develops at once if furfural is present. It is not specific for furfural, since 5-methylfurfural and 5-hydroxymethylfurfural will also give a positive test.

Procedures for quantitative estimation may be divided into two groups based on (a) the aldehyde group and (b) the ring reactions. The method selected should depend on the nature of the other materials present. The official method of the A.O.A.C. for the determination of pentosans has been most generally employed (1). This involves distillation in the presence of hydrochloric acid under carefully controlled conditions, followed by precipitation of the aldehyde with phloroglucinol (1,3,5-trihydroxybenzene). Considerable practice is required to secure duplicate results; the results obtained range from 98 to 102% of the actual furfural content. A volumetric procedure, based on the reaction of furfural with sodium bisulfite (14), is useful in determining the aldehyde in the presence of other furan compounds, especially furfuryl alcohol. The method of Hughes and Acree is dependent upon the reaction of bromine with the furan ring under carefully controlled conditions of temperature and time (24). It gives results within 1% of the correct value.

Many substances interfere with these furfural determinations. Sometimes distillation of the furfural from an aqueous solution as called for in the A.O.A.C. method will eliminate the impurities.

#### SOURCES

Typical pentosan-containing raw materials which can be used for furfural production and which average 12–22% potential furfural are shown in Table III (23). There are many other potential furfural-yielding materials, but in general the yields are lower than from the materials listed in Table III. The factors influencing the choice of raw material are delivered price, availability, cost of conversion, and the value of by-products produced.

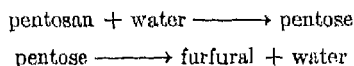
TABLE III. Typical Potential Furfural Yields from Possible Raw Materials.

Raw material	Furfural obtained (dry basis) by A.O.A.C. method, %	Raw material	Furfural obtained (dry basis) by A.O.A.C. method, %
Cleaned oat hulls.....	22	Bagasse.....	17
Corncoobs.....	22	Oak tanbark.....	13
Cottonseed hull bran.....	20	Rice hulls.....	12
Cornstalks.....	16.5	Flax shives.....	14
Buckwheat hulls.....	17	Peanut hulls.....	12

Corncoobs are an abundant source, with an average production in the U.S. of about 16,000,000 tons annually. This is equivalent to more than 1,500,000 tons of furfural, many times the present market. In addition to corncoobs, cottonseed hull bran, oat hulls, and rice hulls are used commercially.

#### MANUFACTURE

The manufacture of furfural is based on the following reactions:



Commercially, furfural is produced in a single-step operation. The raw material is charged to large rotary digesters and treated with dilute sulfuric acid. The furfural formed is removed by steam distillation. The vapors leaving the digesters are condensed and fed to a stripping column. Overhead vapors, rich in furfural, are condensed and cooled, separating into two layers. After removal of a small quantity of low-boiling heads in a methanol column, the water layer is returned to the stripping column for recovery of furfural. The furfural layer containing about 6% water is sent to the dehydrating column, where the water is taken overhead, and dry furfural is drawn from the base. Distillate from the dehydrating column is sent to the stripping-column decanter for recycling through the system. Dunning and Lathrop have proposed the removal of xylose from the other constituents before ring closure (15). Regardless of the process used, the controlling factors of the digestion step are the liquid-solid ratio, time, temperature, and acid concentration. For further details on the process see reference (23).

A typical analysis of furfural is as follows: furfural, 99.5%; moisture, 0.02%; acidity, 0.015 equivalent per liter;  $b_{744}$  (Todd still) 98% over, 160°C. Furfural is shipped in 1-, 5-, and 10-gal. cans, 55-gal. drums, and tank cars. The price in tank-car lots was 9½¢/lb. in October 1950.

#### HEALTH AND SAFETY FACTORS

Many years of practical experience, both in furfural-manufacturing plants and in user's plants, demonstrate conclusively that under ordinary plant conditions the use of furfural is not hazardous to the health of employees. Exhaustive physical examinations of workers in daily contact with furfural for as long as ten years disclosed no instance of personal injury or impairment of health. Nevertheless, ordinary common-sense precautions should be observed. As in the case of gasoline, turpentine, and other well-known industrial solvents, adequate ventilation should always be provided. Furfural should not be allowed to remain in contact with the skin, as it may be a local irritant. If spilled on the body, it should be washed off with water. It will stain the skin yellow-brown if in contact with it for any considerable time. If furfural is likely to come in contact with the hands, rubber or neoprene gloves are recommended.

Due to the relatively high boiling point of furfural (323°F.), it is difficult to build up substantial concentrations in the atmosphere. Its odor is usually sufficient warning of its presence, but chemical tests using color reactions of furfural with aniline acetate have been devised (27). Flammability of furfural is comparable to that of kerosene or No. 1 fuel oil, and may be controlled by the use of water, foam, carbon dioxide, or dry chemicals.

#### USES

*Chemical Intermediate.* The most recent and largest individual commercial use of furfural is that of a chemical intermediate. The production of nylon involves the conversion of furfural to furan and then tetrahydrofuran, which is subjected to ring-opening conditions to produce 1,4-dichlorobutane (see Vol. 3, p. 777). Sodium cyanide converts this to adiponitrile,  $\text{CN}(\text{CH}_2)_4\text{CN}$ , which is hydrogenated to hexamethylenediamine,  $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$  (5). High-pressure hydrogenation of furfural in the liquid phase using a copper oxide-chromium oxide catalyst yields furfuryl alcohol (see p. 1003), which in turn can be hydrogenated to the saturated alcohol (see p. 1004).

Many other compounds of industrial importance or potential importance may be

produced from furfural, typical ones being an essential amino acid, lysine (7), pyrrole, pyrrolidine, methylfuran, methyltetrahydrofuran, dihydropyran, levulinic acid, 1,5-pentanediol (pentamethylene glycol), piperylene (1,3-pentadiene), tetrahydrofurfuryl oleate, pyridine, furoic acid, and hydrofuramide.

*Selective Solvent in the Refining of Oils.* In the solvent refining of lubricating oils to increase the stability under operating conditions and to improve the viscosity-temperature relationship, furfural is one of the most widely used solvents (38). Mineral oils processed range from Diesel fuel to heavy lubricating-oil stocks of over 200 Saybolt Universal seconds viscosity at 210°F. The extracted oil output of individual plants varies from 60 to 10,000 bbl. per day, while the stocks processed include naphthenic and paraffinic distillates and residues.

The furfural refining process involves extraction of raw lubricating stock with furfural at temperatures up to 450°C. (max.) to yield a refined oil and an extract (26). The undesirable aromatic and olefinic components of the oil are selectively dissolved by the furfural and thereby separated from the desirable paraffinic and naphthenic components. Oil enters near the bottom of a countercurrent extraction column and furfural is applied at a point near the top. The extract is removed from the bottom of the column with the bulk of the furfural. The furfural losses are generally 0.02% or less per cycle. See also *Lubrication and lubricants*.

Natural glyceride (fatty) oils may be separated into two or more different fractions by the use of furfural as a solvent in an operation similar to that used for refining mineral oils (19). Although the process has been used chiefly to make separations based on degree of unsaturation within a glyceride mixture, it may also be used to fractionate fatty acids, concentrate valuable minor ingredients of oils, or separate compounds of different molecular weight.

*Resin Former.* Furfural and phenol react readily to form fusible soluble resins, which may be converted to infusibility by heat in the presence of catalysts such as hexamethylenetetramine. Phenol-furfural condensation products have found their most extensive application in the two-stage form. They are characterized by long flow properties and rapid cure at curing temperatures of 330-350°F. Long flow properties are useful in forming operations on large parts or complicated molds where thin sections aggravate the problem of precure (30). Furfural-phenol resins are also useful in the form of varnishes and as resin binders. In some cases the use of furfural results in improved resistance of the cured phenolic resin toward acids and moisture. See also *Phenol resins and plastics*.

*Decolorizing Agent for Wood Rosin.* Furfural is used to remove color bodies from crude FF grade wood rosin to produce a light-colored product capable of competing with gum rosin, which is used in the soap, varnish, and paper industries. After removal by fractional steam distillation of most of the color bodies producing the characteristic ruby red color of crude rosin, the other type of color bodies, which react with alkali to produce red products, are extracted with furfural from a solution of the crude rosin in warm gasoline. Since furfural and gasoline are almost entirely immiscible at low temperatures, a furfural-gasoline-rosin solution separates into two layers on cooling. A light-colored rosin is obtained on evaporation of the gasoline layer, and the furfural is recovered by distillation of the other layer (25).

By adjusting the operating conditions it is possible to produce rosin to conform to any grade on the American scale up to X grade. See also *Rosin and rosin derivatives*.

*Reactive Solvent in the Manufacture of Resinoid-Bonded Grinding Wheels.* For



many years resin-bonded abrasive wheels have been made with furfural. In the manufacture of cold-molded grinding wheels, the abrasive grain is wetted with furfural, or a solvent mixture containing furfural, followed by addition of the desired amount of pulverized phenolic resin. See also *Abrasives*, Vol. 1, p. 10.

*Extractant for Butadiene.* Butadiene is one of the principal components of GR-S general-purpose synthetic rubber. Furfural, although not present in the finished GR-S rubber, is used as an extractive distillation medium in one of the principal processes for the manufacture of butadiene from petroleum. The furfural losses are extremely small (0.01–0.02% of the circulation rate). Hydrocarbons with four carbon atoms, such as *n*-butane, isobutane, 1-butene, 2-butene, and butadiene, have similar boiling points but widely different solubility characteristics. When distillation of the mixtures is carried out in the presence of furfural, the relative volatility of the several C<sub>4</sub> hydrocarbons is altered sufficiently for ready separation (4). See also *Rubber, synthetic*.

### Furfuryl Alcohol

Furfuryl alcohol (2-furanmethanol (C.A.), fureylcarbinol), C<sub>4</sub>H<sub>3</sub>OCH<sub>2</sub>OH, formula weight 98.10, is a water-white liquid that gradually turns amber to almost black in the presence of air. It is soluble in water and in many common organic solvents. Furfuryl alcohol was prepared in the laboratory as early as 1864 by the reduction of furfural with sodium amalgam. High-pressure catalytic hydrogenation was developed by Peters, and by Adkins and Connor so that furfuryl alcohol became commercially available in 1934. Its chief uses are as a resin former and as a solvent.

#### PHYSICAL AND CHEMICAL PROPERTIES

Some of the physical properties are given in Table I. Additional properties are as follows: m.p. (metastable form), –29°C.; vapor pressure:

Temperature, °C.....	40	60	80	100	120	140
Vapor pressure, mm. Hg....	1.8	6.3	20.3	53.5	127.4	271.0

sp.heat of liquid at 0°C., 0.472 cal./(gram)(°C.); heat of fusion, 31.8 cal./gram; heat of combustion of liquid to yield water and carbon dioxide at 25°C., at constant volume 6,206.6 cal./gram, at constant pressure 6,209.6 cal./gram; free energy of formation ( $\Delta F_f^0$ ) of liquid at 25°C., –36,880 cal./gram-mole; entropy of formation ( $\Delta S_f$ ) of liquid from elements at 25°C., –97.86 cal./(gram-mole)(°C.); enthalpy of formation ( $\Delta H_f^0$ ) of liquid from graphitic carbon, hydrogen, and oxygen at 25°C., –66,060 cal./gram-mole; entropy (*S*) of liquid at 25°C., 51.58 cal./(gram-mole)(°C.).

Industrial-grade furfuryl alcohol is amber in color and completely miscible with water at temperatures above 21°C. It is stored and handled in steel without any special precautions. During storage it gradually becomes less soluble in water due to intermolecular dehydration (12), which is accelerated by heat and/or acidic materials and may be retarded by addition of small amounts of organic or inorganic bases.

Deterioration of furfuryl alcohol due to autoxidation is indicated by the development of color, acidity, and increased moisture content. It may be inhibited by the addition of tri-*n*-propylamine or other basic material, or it may be prevented by the elimination of oxygen. Tri-*n*-propylamine causes an initial slight darkening of the furfuryl alcohol, but thereafter the color remains unaltered for extended periods, even on exposure to oxygen.

The most important industrial reaction of furfuryl alcohol is resinification in the

presence of acids. The reaction is highly exothermic and has a high temperature coefficient, so that adequate means for removal of heat must be provided. The reaction may be stopped at any desired point by cooling and neutralization of the catalyst (12). The mechanism of resinification of furfuryl alcohol is complex and has not been completely explained. It has been established that the initial action is one of intermolecular dehydration (12). As resinification proceeds, formaldehyde is evolved; di- $\alpha$ -furylmethane (2,2'-methylenedifuran) has been identified as an intermediate product (33). Accompanying the resinification, particularly when carried out in a dilute aqueous medium, is a ring cleavage reaction leading to the formation of levulinic acid,  $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COOH}$ . Under certain conditions this becomes the major reaction, giving a 64% yield of levulinic acid (2).

As a primary alcohol, furfuryl alcohol can be used for esterification of various carboxylic acids. However, because it readily resinifies in the presence of strong acids, esterification is best carried out by the comparatively mild techniques of ester interchange.

#### MANUFACTURE

Furfural is hydrogenated at 1000–1500 p.s.i. at 175°C., in the presence of copper oxide–chromium oxide catalyst to yield furfuryl alcohol (36). Under these conditions this catalyst is selective and does not promote hydrogenation of the furan ring. Furfuryl alcohol is shipped in 1-, 5-, and 10-gal. cans, 55-gal. drums, and tank cars. The price in tank-car lots was 18¢/lb. in October 1950.

#### USES

The largest use of furfuryl alcohol is in the manufacture of dark thermosetting resins, which are outstanding because of their resistance to corrosive chemicals, acids, alkalies, and solvents. Usually the furfuryl alcohol is first partially polymerized to a soluble and fusible resin using an acid catalyst, and then neutralized. When neutralized, the resin is storage-stable, but is rendered infusible by adding an acid catalyst at the time of use. These liquid furfuryl alcohol resins are used for tank and digester linings, for making cast molded equipment, in cementing and reinforcing ceramics, and in the production of laboratory-table tops.

Furfuryl alcohol is also an excellent solvent for phenolic resins and a wetting agent for the abrasive grain used to manufacture grinding wheels. In the textile industry, furfuryl alcohol is used as a dye solvent and dispersant for difficultly soluble dyes. Furfuryl alcohol can be hydrogenated to the tetrahydro derivative.

#### Tetrahydrofurfuryl Alcohol

Tetrahydrofurfuryl alcohol,  $\text{C}_4\text{H}_7\text{OCH}_2\text{OH}$ , formula weight 102.13, is a high-boiling liquid with a mild pleasant odor. It is completely miscible with water. The commercial product is almost water-white and is handled and shipped in steel. On exposure to oxygen (air) in iron or copper containers, tetrahydrofurfuryl alcohol discolors slowly, but it is not discolored when stored in contact with aluminum, even over an extended period of time.

Some of the physical properties are given in Table I. Additional properties are as follows: heat of combustion, 709.5 kg.-cal./gram-mole; flammability limits, 72.5–122°C., 1.5–9.7%; dielectric constant at 23°C., 37.1.

Tetrahydrofurfuryl alcohol is prepared by liquid-phase hydrogenation of furfuryl alcohol over a nickel catalyst. It is shipped in 1-, 5-, and 10-gal. cans, 55-gal. drums, and tank cars. The price in tank-car lots was 38¢/lb. for the pure grade and 26½¢/lb. for the industrial grade in October 1950.

Tetrahydrofurfuryl alcohol is used in the preparation of esters, particularly tetrahydrofurfuryl oleate, which is almost colorless and has excellent light and heat stability. It is used as a secondary plasticizer with dioctyl phthalate for polyvinyl chloride films. Tetrahydrofurfuryl alcohol is a solvent for: cellulose acetate, cellulose nitrate, ethyl cellulose, furfuryl alcohol polymers, styrene, phenol-aldehyde resins, and vinyl acetate. Another growing use of tetrahydrofurfuryl alcohol is as a chemical intermediate. Dehydration gives 3,4-dihydro-2H-pyran (2,3-dihhydropyran),  $\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} : \text{CH}$ ,

which is the base for a series of interesting new compounds among which are lysine, 1,5-pentanediol, 1,5-dichloropentane (see Vol. 3, p. 780), and tetrahydropyran (6). In the United Kingdom, tetrahydrofurfuryl acetate has been used as a lipstick ingredient, based on the high solubility of eosin in it and its compatibility with other components of the lipstick.

### Furan

Furan (furfuran),  $\text{C}_4\text{H}_4\text{O}$ , formula weight 68.07, is a colorless liquid with a mild pleasant odor.

*Physical Properties.* Some of the physical properties are given in Table I. Additional properties are: heat of vaporization at 31.2°C., 95.5 cal./gram; heat of combustion at constant volume, 500.1 kg.-cal./gram-mole; heat of formation, 14.8 kg.-cal./gram-mole.

The solubility of furan in water at 25°C. is 1 gram per 100 grams of water; the solubility of water in furan at 25°C. is 0.3 gram per 100 grams furan. Furan is miscible with ethyl acetate, methanol, ethyl alcohol, isobutyl alcohol, *n*-amyl alcohol, acetone, methyl ethyl ketone, ethyl ether, heptane, petroleum ether, benzene, toluene, trichloroethylene, methylene chloride, and chloroform. It is soluble in ethylene glycol to the extent of about 12% by weight.

*Chemical Reactions.* Furan is relatively stable toward heat, although at 670°C. in the absence of a catalyst, or at 360°C. in the presence of nickel, it decomposes to form a mixture consisting mainly of carbon monoxide, together with small amounts of acetylene, ethylene, propylene, methane, butadiene, and other hydrocarbons. Substitution and addition reactions can be effected under the proper conditions, with the reaction taking place first in the 2,5-positions.

Furan reacts with ammonia and with hydrogen sulfide at 450°C. over strong dehydration catalysts such as aluminum oxide to give pyrrole,  $\text{NH} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CH}$ , and thiophene,  $\text{S} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CH}$ , respectively. Furan may be acylated using the Friedel-Crafts reaction, alkoxyated, and caused to undergo the Diels-Alder diene synthesis.

Furan may be hydrogenated to tetrahydrofuran by using hydrogenation catalysts in either the liquid or vapor phase. Reduction by hydrogen with a Raney nickel catalyst at 80°C. gives about 90% yield of tetrahydrofuran. Furan may be catalytically oxidized in the vapor phase with oxygen-containing gases to maleic acid and maleic anhydride.

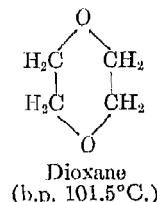
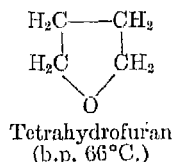
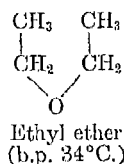
**Manufacture.** Furan is manufactured from furfural by passing a mixture of furfural vapor and steam over catalysts such as a mixed chromite of zinc and manganese at 400°C. (5,39). It can also be prepared by the decarboxylation of 2-furoic acid or dehydration of succinaldehyde,  $\text{OCHCH}_2\text{CH}_2\text{CHO}$ , in its enol form.

**Health and Safety Factors.** If not handled properly, furan is a potentially hazardous chemical for industrial use (28). The concentration of furan in the atmosphere should be kept to a minimum, and skin contact with liquid furan should be avoided in order to prevent possible local and systemic effects. It is recommended that workers with any abnormal circulatory, gastrointestinal, or liver conditions should not be exposed to furan.

Because of the low boiling point, low flash point, and high flammability of furan, it should be kept away from heat and open flame. Unstabilized furan on exposure to the air slowly forms an unstable peroxide. Consequently precautions should be used in distilling this material.

### Tetrahydrofuran

Tetrahydrofuran (tetramethylene oxide),  $\text{C}_4\text{H}_8\text{O}$ , formula weight 72.10, is a colorless liquid with an etherlike odor. It is a saturated cyclic ether, which is a solvent for high-molecular polyvinyl chloride, polyvinylidene chloride, and other difficultly soluble organic materials. The relationship of its structure and boiling point to ethyl ether and dioxane is as follows:



### PHYSICAL AND CHEMICAL PROPERTIES

**Constants.** For some physical properties see Table I. The vapor pressure at different temperatures is:

Temperature, °C.....	25	45	65
Vapor pressure, mm. Hg....	176	385	760

Tetrahydrofuran is miscible with most organic solvents and with water in all proportions. It forms an azeotropic mixture with 4.3% water, and this mixture is a better solvent than tetrahydrofuran for cellulose acetate. Mixtures of water and tetrahydrofuran are more effective as solvents for alkaloids such as caffeine than either water or tetrahydrofuran.

**Reactions.** Tetrahydrofuran has reaction characteristics similar to those of an aliphatic ether, modified by its cyclic structure(28). It can be chlorinated at moderate temperatures under the influence of light to yield primarily 2,3-dichlorotetrahydrofuran. When boiling tetrahydrofuran is treated with gaseous hydrogen chloride, it is converted to 4-chlorobutanol. Further heating of the 4-chlorobutanol with hydrogen chloride in the liquid phase to 110°C. under pressure produces 4,4'-dichlorodibutyl ether. 1,4-Dichlorobutane can be readily prepared by passing a mixture of tetrahydrofuran and hydrogen chloride through a reactor maintained at 180°C. and 15–20 atm. pressure.

Like a number of other compounds having similar structures, tetrahydrofuran forms an unstable explosive peroxide when it is exposed to air. For this reason, commercial tetrahydrofuran is stabilized with an antioxidant such as hydroquinone before it is shipped. Tetrahydrofuran should not be distilled or evaporated without testing for peroxides (liberation of iodine from an acidified potassium iodide solution) and removing them, if present, by treatment with a mixture of ferrous sulfate heptahydrate and sodium hydrogen sulfate(28). Oxidation of tetrahydrofuran with air or oxygen in the presence of a cobalt catalyst (120°C. and 100–200 p.s.i. pressure) gives butyrolactone. Tetrahydrofuran can be oxidized to succinic acid by treatment with 50–75% nitric acid or higher oxides of nitrogen at 20–40°C.

The diacetate of 1,4-butanediol is formed by treating tetrahydrofuran with acetic anhydride. Treatment with acyl chlorides gives the corresponding 4-chlorobutyl esters of the aliphatic acids. Tetrahydrofuran reacts with ammonia at 400°C. in the presence of aluminum oxide to form pyrrolidine,  $\text{NH}.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.$

Treatment with hydrogen sulfide over aluminum oxide at 400°C. produces tetrahydrothiophene.

#### MANUFACTURE

Tetrahydrofuran is manufactured by catalytic hydrogenation of furan, which in turn is prepared by catalytic decarbonylation of furfural. It is available in commercial quantities, and is shipped in 1–5-gal. cans, 55-gal. drums, and tank cars.

Because of the low boiling point, low flash point, and high flammability of tetrahydrofuran, it is necessary that the material be kept away from heat and open flame.

The concentration of tetrahydrofuran in the atmosphere should be kept under 100 p.p.m. for an 8-hour exposure. The safe upper limit of concentration has not been established for man, but chronic exposure of dogs to 200 p.p.m. has produced detectable circulatory disturbances.

#### USES

Tetrahydrofuran is used as an intermediate in the preparation of a number of organic chemicals by means of the reactions outlined above. It is also used in large quantities as a solvent for high-molecular polyvinyl chloride and polyvinylidene chloride in the preparation of printing inks, adhesives, lacquers, and other coating compositions. Tetrahydrofuran is an excellent medium in which to carry out Grignard, sodium acetylide, and lithium aluminum hydride reactions. It is also used alone or in combination with water or other solvents as an extractant for physiologically active materials.

#### Furoic Acid

Furoic acid (2-furoic acid, 2-furancarboxylic acid, pyromucic acid),  $\text{C}_4\text{H}_3\text{O}_3\text{COOH}$ , formula weight 112.08, when pure, is a white crystalline solid, m.p. 132°C. The vapor pressure is as follows:

Temperature, °C.....	96	105	118	129	139
Vapor pressure, mm. Hg.....	1.75	3.1	7.05	14.25	26.0

The solubility in water is as follows:

Temperature, °C.....	20	45	65	80
Soly., g./100 ml. water.....	3.6	13.5	147	330

Furoic acid is soluble in alcohol and ether, and insoluble in paraffinic hydrocarbons. The ionization constant is reported as  $7.1 \times 10^{-4}$ .

Furoic acid is obtained from furfural by catalytic oxidation in a basic medium. The carboxyl group attached directly to the ring in furoic acid stabilizes it. The lower alkyl furoates have been prepared in good yields from the acid and the corresponding alcohol by using hydrochloric or sulfuric acid as catalyst. *Furoyl chloride*,  $\text{C}_4\text{H}_3\text{OCOCl}$ , m.p.  $0^\circ\text{C}$ ., b.p.  $176^\circ\text{C}$ ., an important intermediate, is made by treating furoic acid with phosphorus pentachloride, thionyl chloride, or phosgene. *2-Furamide* (2-furoamide),  $\text{C}_4\text{H}_3\text{OCONH}_2$ , m.p.  $142^\circ\text{C}$ ., and many of its derivatives have also been prepared. Decarboxylation of furoic acid gives furan. Furoic acid can be nitrated or sulfonated directly without serious decomposition. Catalytic hydrogenation yields the saturated acid, tetrahydrofuroic acid.

Furoic acid is used as a bactericide and preservative, as well as for the preparation of esters used as flavors and perfume ingredients. Small quantities are employed in textile processing.

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H. J. BARRETT (Tetrahydrofuran)

